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## THE CHEMISTRY OF FUNCTIONAL GROUPS

*A series of advanced treatises under the general editorship of  
Professor Saul Patai*

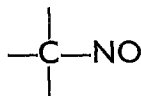
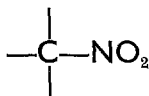
The chemistry of alkenes (published)

The chemistry of the carbonyl group (published)

The chemistry of the ether linkage (published)

The chemistry of the amino group (published)

The chemistry of the nitro and nitroso groups (published in 2 parts)



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# The chemistry of the nitro and nitroso groups

*Edited by*

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Part 1

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# The Chemistry of Functional Groups

## Preface to the Series

The series 'The Chemistry of Functional Groups' is planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. For instance, the volume *The Chemistry of the Ether Linkage* deals with reactions in which the C—O—C group is involved, as well as with the effects of the C—O—C group on the reactions of alkyl or aryl groups connected to the ether oxygen. It is the purpose of the volume to give a complete coverage of all properties and reactions of ethers in as far as these depend on the presence of the ether group, but the primary subject matter is not the whole molecule, but the C—O—C functional group.

A further restriction in the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors is asked *not* to give an encyclopedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced post-graduate level.

With these restrictions, it is realized that no plan can be devised for a volume that would give a *complete* coverage of the subject with *no* overlap between the chapters, while at the same time preserving the readability of the text. The Editor set himself the goal of attaining *reasonable* coverage with *moderate* overlap, with a minimum of

cross-references between the chapters of each volume. In this manner, sufficient freedom is given to each author to produce readable quasimonographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter dealing with the general and theoretical aspects of the group.

(b) One or more chapters dealing with the formation of the functional group in question, either from groups present in the molecule, or by introducing the new group directly or indirectly.

(c) Chapters describing the characterization and characteristics of the functional groups, i.e. a chapter dealing with qualitative and quantitative methods of determination including chemical and physical methods, ultraviolet, infrared, nuclear magnetic resonance, and mass spectra; a chapter dealing with activating and directive effects exerted by the group and/or a chapter on the basicity, acidity or complex-forming ability of the group (if applicable).

(d) Chapters on the reactions, transformations and rearrangements which the functional group can undergo, either alone or in conjunction with other reagents.

(e) Special topics which do not fit any of the above sections, such as photochemistry, radiation chemistry, biochemical formations and reactions. Depending on the nature of each functional group treated, these special topics may include short monographs on related functional groups on which no separate volume is planned (e.g. a chapter on 'Thioketones' is included in the volume *The Chemistry of the Carbonyl Group*, and a chapter on 'Ketenes' is included in the volume *The Chemistry of Alkenes*). In other cases, certain compounds, though containing only the functional group of the title, may have special features so as to be best treated in a separate chapter as e.g. 'Polyethers' in *The Chemistry of the Ether Linkage*, or 'Tetraaminoethylenes' in *The Chemistry of the Amino Group*.

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, it was decided to publish certain volumes in several parts, without giving consideration to the originally planned logical order of the chapters. If after the appearance of the originally



planned parts of a volume, it is found that either owing to non-delivery of chapters, or to new developments in the subject, sufficient material has accumulated for publication of an additional part, this will be done as soon as possible.

It is hoped that the series 'The Chemistry of Functional Groups' will include the titles listed below:

- The Chemistry of the Alkenes (published)*
- The Chemistry of the Carbonyl Group (published)*
- The Chemistry of the Ether Linkage (published)*
- The Chemistry of the Amino Group (published)*
- The Chemistry of the Nitro and Nitroso Groups (published)*
- The Chemistry of Carboxylic Acids and Esters (in press)*
- The Chemistry of the Carbon-Nitrogen Double Bond (in preparation)*
- The Chemistry of the Cyano Group (in preparation)*
- The Chemistry of the Carboxamido Group (in preparation)*
- The Chemistry of the Carbon-Halogen Bond*
- The Chemistry of the Hydroxyl Group (in preparation)*
- The Chemistry of the Carbon-Carbon Triple Bond*
- The Chemistry of the Azido Group*
- The Chemistry of Imidoates and Amidines*
- The Chemistry of the Thiol Group*
- The Chemistry of the Hydrazo, Azo and Azoxy Groups*
- The Chemistry of Carbonyl Halides*
- The Chemistry of the SO, SO<sub>2</sub>, —SO<sub>2</sub>H and —SO<sub>3</sub>H Groups*
- The Chemistry of the —OCN, —NCO and —SCN Groups*
- The Chemistry of the —PO<sub>3</sub>H<sub>2</sub> and Related Groups*

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editor.

The publication of this series would never have started, let alone continued, without the support of many persons. First and foremost among these is Dr. Arnold Weissberger, whose reassurance and trust encouraged me to tackle this task, and who continues to help and advise me. The efficient and patient cooperation of several staff-members of the Publisher also rendered me invaluable aid (but unfortunately their code of ethics does not allow me to thank them by name). Many of my friends and colleagues in Jerusalem helped

me in the solution of various major and minor matters and my thanks are due especially to Prof. Y. Liwschitz, Dr. Z. Rappoport and Dr. J. Zabicky. Carrying out such a long-range project would be quite impossible without the non-professional but none the less essential participation and partnership of my wife.

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SAUL PATAI

# Foreword

The concept of this book arose from several discussions with Professor Saul Patai during my sabbatical leave at the Hebrew University of Jerusalem in the Spring of 1964. While disclosing his plans to edit a series of treatises concerned with the chemistry of functional groups, inclusion of the nitro and nitroso groups as the subject-matter for one of the volumes was brought forward. I accepted the editorship of such a treatise as part of the series because I considered it very worthwhile that up-to-date discussions on the theoretical, physical, and mechanistic aspects of these groups be unified in one publication, by active workers in the field. For although several review articles, proceedings of various symposia, and isolated chapters in various books have concerned themselves with certain aspects of the chemistry of the nitro and nitroso groups—an active and exciting field of research—no self-contained book on the subject has been available.

As in the already published books of this series, the subject-matter in this treatise has been considered from the viewpoint of the functional group. Instead of an encyclopedic coverage of all known reactions and compounds, the emphasis has been placed on basic principles, mechanisms, and recent advances in both theory and practice. It is hoped that by choosing this approach, a broad and concise picture of the importance of the nitro and nitroso groups has been attained.

The editing and publishing of a book which is made up of contributions from several authors are usually delayed by the fact that the deadline agreed upon is exceeded by some of the contributors. Such delay is unfortunate because it can sometimes result in obsolescence of some parts of a manuscript. To minimize such possibilities, which invariably occur when discussions in active fields of research are involved, and to keep the format of the book to a manageable size, it was decided to publish the treatise in two volumes.

It is with great pleasure that I acknowledge the cooperation of Professor Saul Patai, and the advice and suggestions in editorial matters of the Publishers. I also express my gratitude to Mr. M. Auerbach who did most of the painstaking work involved in preparing the Subject Index.

Lafayette, December 1968

HENRY FEUER

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# Contents—Part I

1. Theoretical aspects of the C—NO and C—NO <sub>2</sub> bonds George H. Wagnière	1
2. Spectroscopy of the nitro group C. N. R. Rao	79
3. Spectroscopy of the nitroso group C. N. R. Rao and K. R. Bhaskar	137
4. The photochemistry of the nitro and nitroso groups Harry A. Morrison	165
5. Methods of formation of the nitroso group and its reactions J. H. Boyer	215
6. Methods of formation of the nitro group in aliphatic and alicyclic systems H. O. Larson	301
7. Nitronic acids and esters Arnold T. Nielsen	349
8. Activating effects of the nitro group in nucleophilic aromatic substitutions Th. J. de Boer and I. P. Dirks	487
9. Methods of formation of the nitramino group, its properties and reactions George F Wright	613
Author Index	685
Subject Index	735

# **Contents—Part 2**

**Methods of formation of the nitro group in aromatic systems**

W. W. Weaver

**Directing effects of the nitro group in electrophilic and radical aromatic substitutions**

T. Urbanski

**Directing and activating effects of the nitro group in aliphatic and alicyclic systems**

H. H. Baer

**Syntheses and reactions of trinitromethyl compounds**

L. A. Kaplan

**Complexes of aromatic nitro compounds, including Meisenheimer and charge-transfer complexes**

T. N. Hall

**Biological formation and reactions of the nitro and nitroso groups**

J. Venulet and R. L. VanEtten

**Author Index**

**Subject Index**

## CHAPTER I

# Theoretical aspects of the C–NO and C–NO<sub>2</sub> bonds

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I. QUANTUM MECHANICAL CALCULATIONS OF MOLECULAR PROPERTIES	2
A. The Molecule as a Many Body Problem	2
1. Some general remarks	2
2. The separation of the motions of electrons and nuclei	3
B. Solution of the Electronic Problem	3
1. The LCAO-MO scheme	4
2. Semiempirical calculations	6
II. ALIPHATIC C–NO AND C–NO <sub>2</sub> COMPOUNDS	7
A. Nitric Oxide and Nitroso Alkanes	7
1. <i>Ab initio</i> calculations on NO	7
2. The physical properties of nitrosoalkanes	10
B. Nitroxides and <i>N</i> -Oxides	15
1. Electronic and magnetic properties of nitroxide radicals	15
a. Nitroxides from amines	15
b. Nitroxides from oximes	21
2. The dative bond in trimethylamine <i>N</i> -oxide	22
C. Nitrogen Dioxide and Nitroalkanes	23
1. The electronic structure of NO <sub>2</sub>	23
a. General discussion. The position of the unpaired electron	23
b. Electron interaction and ionization potentials	25
2. The electronic properties of nitroalkanes	32
3. On the structure of nitroethylene	38
III. AROMATIC C–NO AND C–NO <sub>2</sub> COMPOUNDS	39
A. Ground and Excited State Properties of Nitrobenzene, Nitroso- benzene and Their Derivatives	39
1. The electronic structure of nitrobenzene	39
2. The electronic properties of substituted nitrobenzenes	48

3. The electronic structure of nitrosobenzene and substituted nitrosobenzene . . . . .	51
B. Magnetic Properties of Nitro and Nitroso Aromatic Compounds . . . . .	54
1. Pi-electron density and NMR chemical shifts . . . . .	54
2. The radical anions of nitroaromatic compounds . . . . .	58
C. Aromatic <i>N</i> -Oxides and Nitroxides . . . . .	64
1. The electronic structure of pyridine <i>N</i> -oxide and related compounds . . . . .	64
2. Magnetic properties of aromatic nitroxides . . . . .	68
IV. SOME SPECIAL TOPICS . . . . .	69
A. Vibrational Spectra . . . . .	69
B. Chemical Reactivity . . . . .	70
V. ACKNOWLEDGMENT . . . . .	71
VI. REFERENCES . . . . .	71

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## I. QUANTUM MECHANICAL CALCULATIONS OF MOLECULAR PROPERTIES

### *A. The Molecule as a Many Body Problem*

#### **I. Some general remarks.**

Ever since the birth of quantum mechanics in the mid-nineteen-twenties it has generally been assumed that this branch of theoretical physics should adequately explain all atomic and molecular properties and phenomena commonly designated as 'chemistry'<sup>1</sup>. Quantum chemistry thus starts from the idea that the solution of the Schrödinger equation for any atomic or molecular system should enable one to completely understand its behaviour. The difficulty of quantum chemistry does not lie in writing down the Schrödinger equation for a particular system, but rather in solving it. The complexity of this differential equation rapidly rises with the number of particles involved. Only the equation for the hydrogen atom may easily be solved to a satisfactory degree of accuracy. As soon as we tackle the three body problem, even the best solutions obtained to date have a much more approximate nature. The labor required to find these solutions rapidly becomes immense.

The experimental investigation of matter proceeds along two lines: (*a*) the interaction of atoms and molecules with electromagnetic radiation, commonly called spectroscopy; (*b*) the interaction of atoms and molecules among themselves, which we may call 'kinetics'. Traditionally, spectroscopy rather belongs to



physics, and chemistry is more or less identical with what we here call 'kinetics'. However, the importance of spectroscopy to the understanding of kinetic processes has become so great, that it is difficult to separate these two branches of investigation. Due to the mathematical difficulties outlined above, we cannot rely on calculations alone to gain a deeper understanding of chemical reactions. We are very heavily dependent on the results of spectroscopic measurements. The first and more modest aim of quantum chemistry therefore is to interpret the results of such spectroscopic investigations. In many instances the atom or molecule may then be treated as an isolated system, and the interaction with its surroundings and with radiation as a weak perturbation, which simplifies the problem. Nevertheless, the task is still a formidable one and still requires the introduction of suitable approximations.

Attempts to calculate accurately the reactivity of molecules and the course of chemical reactions quickly lead to intractable mathematical problems. From that point of view predictions are at best tentative and semi-quantitative.

## **2. The separation of the motions of electrons and nuclei**

Already in 1927 Born and Oppenheimer<sup>2</sup> had shown that, due to the great mass difference between the nuclei and electrons, the motions in a molecule of the nuclei may be treated separately from the motions of the electrons. Qualitatively, the picture which emerges is that the slowly moving nuclei see the electrons as a cloud surrounding them and confining their motion to a definite region of space—the rapidly moving electrons see the nuclei as almost static centers around which they evolve. The quantum mechanical problem is thus separated into equations for the electronic properties at fixed nuclear configuration on one hand, and equations for the vibrations of the nuclei from the equilibrium configuration and for the overall rotation of the molecular frame on the other. This first simplification is, however, not yet sufficient by far to make the problem as a whole readily soluble. Our work depends on further approximation.

### **B. Solution of the Electronic Problem**

Our main interest here lies in the properties of the valence electrons, which are responsible for chemical reactions. Although we are unable to give a detailed mathematical treatment of such a

reaction, our interpretation of the spectroscopic properties of valence electrons, and our deductions as to their distribution in space may give useful clues as to their role in chemical binding.

In our case, the bonds C—NO and C—NO<sub>2</sub> are no physical entities. Depending on the molecule to which they belong, our theoretical description may be quite different. In general, the larger the molecule in question, the more drastic the approximations necessary to make calculations tractable.

Firstly, we therefore want to give an outline of the general course of a calculation; secondly, we will deal in some detail with the approximations.

## 1. The LCAO-MO scheme

A method of solution widely adopted in molecular electronic problems is the LCAO-MO (linear combinations of atomic orbitals-molecular orbital) scheme. The main steps of such a calculation are outlined in Table 1. We will assume the reader to be familiar in a qualitative way with the solutions of the Schrödinger equation for the hydrogen atom, the hydrogenic wave functions, or hydrogen

TABLE 1. Various steps in solving the molecular electronic problem, according to the LCAO-MO scheme.

<i>Atomic Orbitals</i> $\chi_1, \chi_2, \dots, \chi_p \dots$	Choice of the initial basis.
<i>Molecular Orbitals</i> $\varphi_i = \sum_p c_{ip} \chi_p; \varepsilon_i$	Variational procedure. One-electron molecular orbitals; one electron energies.
<i>Spinorbitals</i> $\varphi_i \alpha, \varphi_i \beta$	Inclusion of spin.
<i>Slater determinant</i> $\Phi_{\Lambda} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1 \alpha(1) & \varphi_1 \alpha(2) & \cdots & \varphi_1 \alpha(N) \\ \varphi_1 \beta(1) & \varphi_1 \beta(2) & \cdots & \varphi_1 \beta(N) \\ \cdots & \cdots & \cdots & \cdots \\ \varphi_K \beta(1) & \varphi_K \beta(2) & \cdots & \varphi_K \beta(N) \end{vmatrix}$	Many-electron function. Product of one-electron spinorbitals. Antisymmetrized with regards to interchange of electrons.
<i>Solution of the Electronic Problem</i> $\Psi_n = \sum_{\Lambda} A_{n\Lambda} \Phi_{\Lambda}; E_n$ $\Psi_0$ : Ground state wave function, with energy $E_0$ . $\Psi_1, \Psi_2 \dots$ : Excited state wave functions, with energies $E_1, E_2 \dots$	Configuration interaction calculation.

atomic orbitals<sup>3,4</sup>. The electronic structure of many-electron atoms may also be described by using atomic orbitals, which in their 'shape' i.e. angular dependence, are also like hydrogenic orbitals.

Orbitals of the atoms, of which the molecule in question is built up, are combined in a first step to one-electron molecular orbitals. This may be done by a variational procedure and leads to a system of simultaneous algebraic equations (leading to a secular equation) to determine to what extent each atomic orbital will contribute to a given molecular orbital. The question of how many atomic orbitals are to be considered in building up the orbitals of a particular molecule is a matter of appreciation. In general, the more limited this set is, i.e. the smaller the atomic orbital basis, the simpler the computation will be, but also the greater the restrictions imposed on the quality of the results and on any further calculations. Molecular orbitals and their energy eigenvalues give us a first approximate description of the electrons in a molecule, treated as independent entities.

A wave function for the electrons treated collectively can be expressed in terms of the one-electron molecular orbitals. It also has to take into account the spin properties of the electrons and the Pauli principle. Thus every one-electron molecular orbital must be multiplied by a spin function  $\alpha$  or  $\beta$ , corresponding to spin values  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . Furthermore, the function must be antisymmetric with respect to interchange of two electrons and is therefore written as an antisymmetrized product of one-electron molecular orbitals, or Slater determinant.

A given one-electron molecular orbital may be occupied by only one electron of given spin value, that is, at most by two electrons with opposite spin. The totality of electrons in the molecule may be distributed in different ways among the complete set of molecular orbitals. Each such distribution is called a configuration and is described by a different Slater determinant. The ground configuration is the one in which the electrons are distributed over the molecular orbitals of lowest energy.

The complete calculation of the electronic problem, aiming at an accurate description of the different electronic states of a molecule, must take into account explicitly the electrostatic interaction between the electrons. This can be achieved by writing the solution—i.e. the molecular electronic wave function as a linear combination of the Slater determinants of all the possible configurations. Strictly speaking, configurations of the ionized system should be included as well. The determination of the extent to which each configuration

contributes to a given state may again be achieved by a variational procedure. Theoretically there is an infinity of different configurations. In practice we must limit ourselves to a finite number, thereby again restricting the accuracy of our results. But we may, for instance, safely assume that—if we use reasonably good molecular orbitals—the ground state of the molecule will consist principally of the ground configuration and that, on the other hand, configurations of much higher energy will make vanishingly small contributions to it.

The general procedure outlined here leaves room for many modifications. We may optimize the calculation of the one-electron molecular orbitals by taking into account electron interaction to a significant extent already in the first step. We may then obtain SCF (self consistent field) molecular orbitals. The ground configuration expressed in terms of SCF orbitals will be a good approximation to the actual ground electronic state of the molecule<sup>5</sup>. The ground state energy so calculated will be equal to the true energy minus the so-called 'correlation' energy.

We may go to the other extreme, skip the calculation of molecular orbitals, and build up Slater determinants directly from atomic orbitals. We then no longer speak of configurations, but of canonical structures, and our procedure is now no longer called the LCAO-MO, but the VB (valence bond) method<sup>4</sup>.

## 2. Semiempirical calculations

We will now briefly deal with the various degrees of further approximation. Suppose we are studying a large molecule, such as for instance nitrobenzene, the symmetry of which allows us to distinguish between  $\sigma$  and  $\pi$  electrons. In an accurate calculation we would consider the interaction between  $\sigma$  and  $\pi$  electrons explicitly, as well as the interaction between the electrons within a group. Our calculation would start from a large basis of atomic orbitals and all intermediate quantities would be calculated explicitly. We will call this the 'ab initio' procedure. Even on fast present-day computers calculations of this type rapidly become extremely tedious and time consuming for molecules with more than a few atoms. For larger molecules semiempirical procedures become a necessity. They consist in utilizing experimental atomic data, such as ionization potentials and electron affinities in assessing intermediate quantities in the calculation. By the so-called neglect of

differential overlap, for instance, only dominant terms in a calculation are considered, thereby further reducing significantly the amount of labor involved<sup>6,7</sup>. Depending upon the degree of further approximation, we will classify semiempirical calculations into various types.

*Type (a)*: Both  $\sigma$  and  $\pi$  electrons are taken into account. Interaction between all electrons is considered explicitly.

*Type (b)*: Only  $\pi$  electrons are taken into account, interaction between the  $\pi$  electrons is considered explicitly.

*Type (c)*: Both  $\sigma$  and  $\pi$  electrons are taken into account, but their interaction is not treated explicitly. This is the so-called extended Hückel method<sup>8</sup>.

*Type (d)*: Only  $\pi$  electrons are taken into account. Their interaction is not treated explicitly. This is the usual Hückel method of  $\pi$  electron theory<sup>9,10</sup>.

In the next section we will consider molecules of many different sizes and geometries. We will discuss *ab initio* calculations on the molecule NO, but we find that only Hückel (type *d*) calculations have been performed to date on certain nitronaphthalenes.

## II. ALIPHATIC C-NO AND C-NO<sub>2</sub> COMPOUNDS

### A. Nitric Oxide and Nitrosoalkanes

#### I. *Ab initio* calculations on NO

The molecule NO is paramagnetic. The first reason for this lies in the fact that it contains an odd number of electrons, of which one must necessarily have an unpaired spin. In the ground electronic state, designated by the spectroscopic notation  $^2\Pi$ , the molecule also possesses a nonvanishing component of electronic angular momentum around the internuclear axis. Thus we may have two different resulting components of the electronic magnetic moment. In the term designated by  $^2\Pi_{\frac{1}{2}}$  the spin magnetic moment and the magnetic moment arising from the orbital angular momentum cancel each other, whereas in the term  $^2\Pi_{\frac{3}{2}}$  the magnetic moments add. These terms are separated by a very small energy interval of  $120.9\text{ cm}^{-1}$  (0.015 eV), the former lying below the latter. In a sample of gas at very low temperature the  $^2\Pi_{\frac{1}{2}}$  state is practically exclusively populated, leading to an effective magnetic moment of zero. At temperatures for which the multiplet splitting is small compared to  $kT$  both levels contain almost equal numbers of

molecules. With increasing temperature the effective magnetic moment thus tends asymptotically towards the value of two Bohr magnetons. In striking contrast to oxygen, NO consequently does not obey Curie's law<sup>11,12</sup>.

The equilibrium bond length of  $\text{N}^{14}\text{O}^{16}$  is  $1.15 \text{ \AA}^{11}$ , and measurements of the dipole moment<sup>13</sup> by the microwave Stark effect give a value of  $0.16 \text{ D}$  (Debye units), with undetermined sign.

Lefebvre-Brion, Moser and Yamazaki have carried out *ab initio* calculations on NO. In a first calculation<sup>14</sup> they start from an atomic orbital basis consisting of the  $1s$ ,  $2s$ ,  $2p_\sigma$ ,  $2p_\pi$ ,  $2p_\pi$  Slater orbitals for oxygen and nitrogen. The  $2p_\sigma$  orbital has its axis parallel to the molecular axis, the axes of the other  $2p$  orbitals lie perpendicular. Molecular orbitals are calculated by the SCF procedure. However, the fact that the ground configuration corresponds to a non-closed shell has to be taken particularly into account (for further discussion of this point see section II.C.1.). In a second calculation<sup>15</sup> the atomic orbital basis is enlarged and some  $3d$ -functions are added to it. The seven SCF-molecular orbitals of lowest energy are assumed doubly filled, the eighth contains a single electron. These eight molecular orbitals, as given by the first calculation<sup>14</sup>, are depicted in Figure 1. According to their symmetry they may be characterized as  $\sigma$  or  $\pi$ . The  $\pi$  orbitals are linear combinations of atomic orbitals  $2p_\pi$ , respectively  $2p_{\bar{\pi}}$ . They are pairwise degenerate, that is,  $1\pi$  corresponds to the same energy as  $1\bar{\pi}$ ,  $2\pi$  to the same energy as  $2\bar{\pi}$ . The probability of finding the unpaired electron in  $2\pi$  is as great as that of finding it in  $2\bar{\pi}$ , due to the interaction of the two degenerate configurations. Consequently the electronic charge distribution is cylindrically symmetric, as expected from physical intuition. On the other hand, the orbitals  $2\pi$ ,  $2\bar{\pi}$  have a node perpendicular to the molecular axis, while the orbitals  $1\pi$ ,  $1\bar{\pi}$  do not. In the two lowest  $\sigma$  orbitals,  $1\sigma$  and  $2\sigma$ , the electrons are located practically entirely on one atom, in the first case on O, in the second case on N. These electrons hardly contribute to the binding of the molecule and practically belong to the respective atomic cores.

At first glance it seems difficult to correlate the molecular orbital picture with the description familiar to the chemist, in which it is assumed that NO shows one  $\sigma$ , one ordinary  $\pi$  and one three-electron  $\pi$  bond.



This situation may be clarified by examining the 'overlap

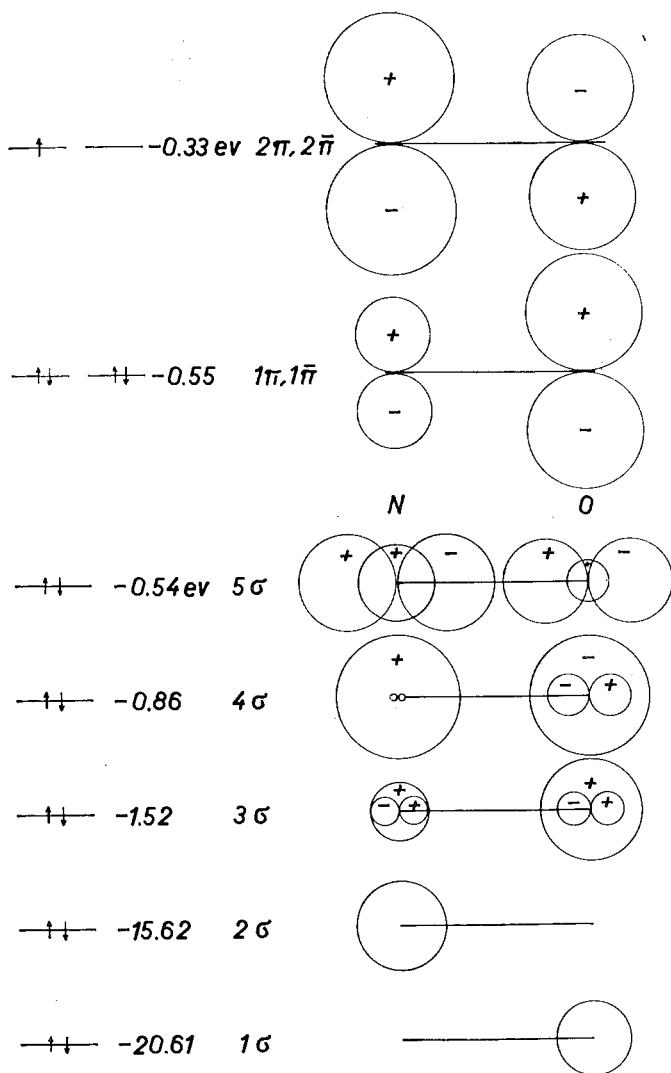


FIGURE 1. The SCF molecular orbitals and eigenvalues for NO, according to the first calculation described in reference 14. The radius of the contour of a given atomic orbital,  $2s$  or  $2p$  is made proportional to the respective LCAO-coefficient. The radii of the  $1s$  orbitals in  $1\sigma$  and  $2\sigma$  are drawn somewhat arbitrarily.

population<sup>\*16</sup> according to Mulliken, which seems a good criterion for assessing the bonding contribution of an electron in a particular orbital. We find the overlap population to be positive, or bonding, in  $3\sigma$ ,  $1\pi$  and  $1\bar{\pi}$ ; approximately zero, or nonbonding, in  $5\sigma$ , negative or antibonding, in  $4\sigma$ ,  $2\pi$ , and  $2\bar{\pi}$ . Thus only six electrons effectively contribute to the binding of the molecule, the two electrons in  $3\sigma$  forming a  $\sigma$  bond, the four electrons in  $1\pi$  and  $1\bar{\pi}$  two  $\pi$  bonds. Effectively, the influence of the unpaired electron is an antibonding one and the picture of the three electron  $\pi$  bond seems somewhat fortuitous. It lets us understand the ease of formation of the positive ion  $\text{NO}^+$ . This is also well reflected by the ionization potential of NO which is 9.25 eV, as compared to 12.2 eV for  $\text{O}_2$ , 15.6 eV for  $\text{N}_2$  and 13.9 eV for  $\text{CO}$ <sup>17</sup>. The antibonding effect of the unpaired electron appears also to influence the bond length, which in  $\text{NO}^+$  is 1.06 Å<sup>18</sup>, thus about 0.09 Å shorter than in NO.

Lefebvre-Brion and Moser make a detailed investigation of the lower electronic states of NO and  $\text{NO}^+$  at various internuclear distances. They also estimate by semiempirical methods the spin-orbit coupling constant, which gives the splitting between the  $^2\Pi_{\frac{1}{2}}$  and  $^2\Pi_{\frac{3}{2}}$  levels of the ground state, obtaining good agreement with experiment. However, in their first calculation they predict a dipole moment  $\text{N}^--\text{O}^+$  of 0.27 D, that is, too large by a factor of almost 2 and with a sign opposite to what one would expect from an electronegativity viewpoint. Unfortunately, this observable does not seem to have been recalculated with the wave functions obtained by the more recent calculation.

Do we find characteristics of the NO molecule in the C—NO bond? What is the charge distribution in this bond? How does the N—O bond length change? Will the C—NO bond show a tendency to be paramagnetic?

We will deal with these questions in the following two sections.

## 2. The physical properties of nitrosoalkanes

The geometry of nitrosomethane does not seem to have been determined experimentally and must be estimated, for instance,

\* The overlap population  $n_i$  of a molecular orbital  $i$  is given by the relation  $n_i = \sum_{rksl} 2N(i)c_{ir}c_{is}S_{rksl}$  where indices  $k$  and  $l$  designate atoms,  $r, s$  orbitals on the respective atoms,  $c_{ir}$  and  $c_{is}$  the coefficients of these atomic orbitals in the  $i$ th MO.  $S_{rksl}$  is the overlap integral between respective atomic orbitals. The summation is carried out over all atomic orbitals in each atom. The expression has to be multiplied by the number of electrons in the molecular orbital,  $N(i)$ .



from data on nitrosyl chloride<sup>19</sup> ( $\angle \text{ClNO} = 116^\circ$ ,  $r_{\text{NO}} = 1.14 \text{ \AA}$ ) and methyl nitrite<sup>20</sup> ( $\angle \text{ONO} = 109.5^\circ$ ,  $r_{\text{ON}} = 1.37 \text{ \AA}$ ,  $r_{\text{NO}} = 1.22 \text{ \AA}$ ). McEwen<sup>21</sup> assumes for nitrosomethane  $\angle \text{CNO} = 120^\circ$ ,  $r_{\text{CN}} = 1.47 \text{ \AA}$ ,  $r_{\text{NO}} = 1.18 \text{ \AA}$  as a basis for semiempirical calculations. An important fact is that one must assume the CNO group to be bent, thereby destroying all properties, such as the degeneracies of the  $\pi$  orbitals, arising from the cylindrical symmetry encountered in NO. However, as the CNO group still has a plane of symmetry, the classification of the molecular orbitals into  $\sigma$  and  $\pi$  orbitals is still justified. McEwen's calculation on nitrosomethane takes into account the  $\sigma$  orbitals, although also in a limited way, neglects differential overlap and may be classified as being of type *a*. Attention is focused on the three highest filled orbitals, of which two are of  $\sigma$  symmetry, designated by  $n$  and  $n^*$  and one is of  $\pi$  symmetry. The lowest unfilled orbital is labeled  $\pi^*$ . The symmetry properties and general shape of these orbitals are shown very schematically in Figure 2. Table 2 gives atomic orbital coefficients, as calculated by McEwen.

Due to the relative instability of nitrosoalkanes, most spectroscopic work has been carried out on perfluoronitrosoalkanes<sup>22</sup>. The electronic spectra of such nitrosoalkanes are best discussed in connection with those of other nitroso compounds (see Table 3.). They are all assumed to show a weakly allowed  $n^*-\pi^*$  transition in the visible, a weakly allowed  $n-\pi^*$  transition in the near UV and a strong  $\pi-\pi^*$  transition in the vacuum UV region.

Instead of viewing the C—N—O group as a physical entity it is perhaps more appropriate in a wider context to divide the molecule into an N—O fragment and a remaining part D. It appears that the spectral characteristics common to these compounds change according to the electron donating properties of D. Even on a qualitative basis one must however distinguish between the capacity of an atom or substituent to donate electrons, primarily related to the ionization potential, and the effects of conjugation, related also to the symmetry and overlapping of atomic orbitals. If D both has a low ionization potential and shows strong effects of conjugation with NO, then intramolecular charge transfer transitions from D to the  $\pi^*$  orbital of NO may occur, as Nagakura and coworkers<sup>23</sup> have shown experimentally and theoretically. The stronger the electron donating effect of D according to these criteria, the lower is the energy of the charge transfer transition.

In contrast to this redshift of the  $\text{D}-\pi^*$  transition, it appears that the  $n^*-\pi^*$  (see Figure 2) transition—which in the alkane and

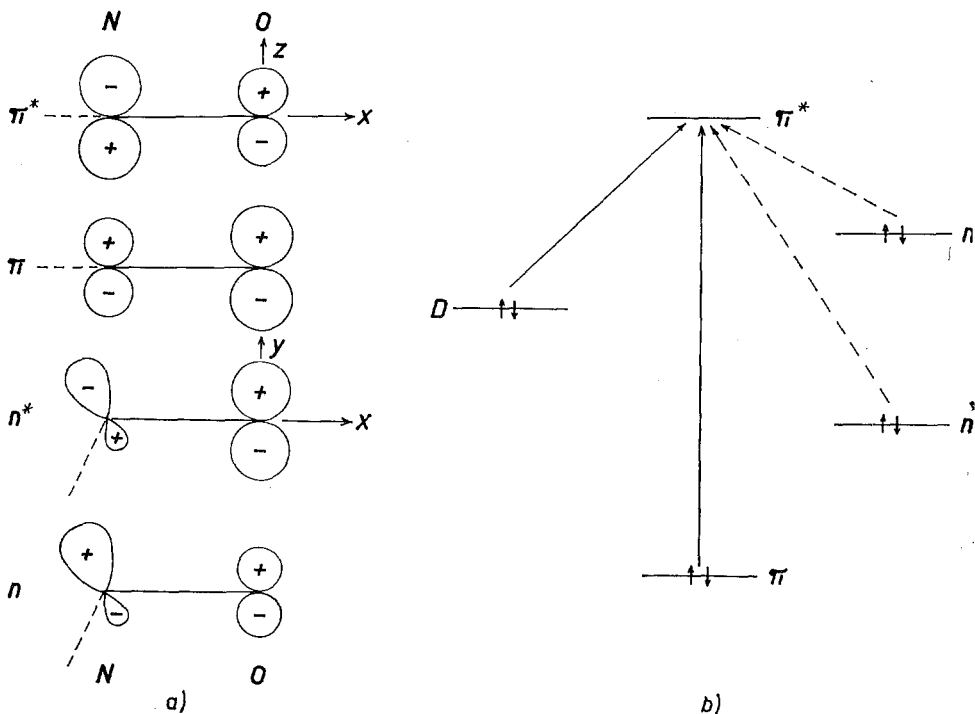


FIGURE 2(a). Simplified picture of the  $\pi$  and nonbonding orbitals of the nitroso group, as it may be applied to nitrosoalkanes.

(b). Qualitative energy level diagram for the nitroso group interacting with an electron donor.

TABLE 2. LCAO-coefficients in MO's of nitrosomethane, according to McEwen<sup>21</sup>.

MO	AO	O <sub>y</sub>	N <sub>y</sub>	O <sub>z</sub>	N <sub>z</sub>	N <sub>s</sub>	C	O <sub>z</sub>	N <sub>z</sub>
$n$		-0.617	-0.592	-0.220	0.325	-0.307	0.141		
$\pi$								0.779	0.628
$n^*$		-0.755	0.406	0.131	-0.227	0.298	-0.328		
$\pi^*$								-0.628	0.779

\* O<sub>y</sub> is the 2p<sub>y</sub> orbital of oxygen, N<sub>s</sub> the 2s orbital of nitrogen, etc. The coördinate axes  $x, y, z$  are shown in Figure 2. C is a collective symbol for contributions from atomic orbitals of the carbon atom. Contributions from the carbon atom are relatively small and those from the hydrogen atoms are here neglected.

TABLE 3. Spectral characteristics of nitroso compounds in the gas phase. Wavelengths of transitions in  $m\mu$  are shown with oscillator strengths ( $f$ -values; for definition see section III.A.1.).  $I(D)$  is the ionization potential of the substituent  $D$ .

Substituent $D$	$I(D)$ eV	$\pi-\pi^*$		$D-\pi^*$		$n-\pi^*$		$n^*-\pi^*$	
		$\lambda(m\mu)$	$f$	$\lambda(m\mu)$	$f$	$\lambda(m\mu)$	$f$	$\lambda(m\mu)$	$f$
CF <sub>3</sub>	obs. 13.84 <sup>c</sup>	not yet obs.		—	—	270 <sup>a*</sup>	0.00005 <sup>a</sup>	690 <sup>a</sup>	0.0002 <sup>a</sup>
	calc.					196 <sup>b</sup>	0.01 <sup>b</sup>	596 <sup>b</sup>	0.002 <sup>b</sup>
C <sub>3</sub> F <sub>7</sub>	obs.	not yet obs.		—	—	hidden?		680 <sup>a</sup>	0.0002 <sup>a</sup>
1-chlorocyclohexyl	obs.	~160	‡	179†		197†		750	$\epsilon_{\max} \sim 0.6$
Cl	obs. 12.84	145	‡	197	‡	hidden?		615	$\epsilon_{\max} \sim 0.7$
(nitrosylchloride)	calc.	143	0.263	197	0.263				
CH <sub>3</sub> —O	obs. 10.85	165	‡	210	0.052	hidden?		386	$\epsilon_{\max} \sim 10$
	calc.	125	0.270	230	0.272				
(CH <sub>3</sub> ) <sub>2</sub> N	obs. 8.24	165		227	0.150	hidden?		377	$\epsilon_{\max} \sim 50$
	calc.	116	0.194	263	0.253	174 <sup>b</sup>	0.02 <sup>b</sup>	417 <sup>b</sup>	0.002 <sup>b</sup>

<sup>a</sup> J. Mason, reference 22.<sup>b</sup> K. L. McEwen, reference 21.<sup>c</sup> Reference 17.

Other data is from M. Tanaka, J. Tanaka, and S. Nagakura, reference 23.

\* J. Mason assumes this band to have  $n-\pi^*$  character. On energetic grounds McEwen ascribes it to a double  $n^*-\pi^*$  excitation with some  $\pi-\pi^*$  character.

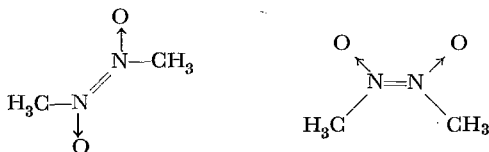
† Assignment uncertain.

‡ Value uncertain.

perfluoroalkane is found at very low frequency—gets simultaneously shifted to the blue, when the electron donating strength of D increases. In a qualitative way, one may say, that the  $D-\pi^*$  and the  $n^*-\pi^*$  configurations compete with each other. The stronger the tendency is for an electron to be transferred from D to  $\pi^*$ , the more energy will be required to promote an electron from  $n^*$  to  $\pi^*$ . A similar phenomenon is observed for the CO group in the series acetaldehyde—acetyl chloride—acetic acid—formamide<sup>23-25</sup>.

As may be expected, the  $n^*-\pi^*$  transition in the nitroso group shows definite sensitivity to the polarity of solvents. On going from the solvent cyclohexane to water there occurs a blue shift in the 680  $m\mu$  absorption of about  $350\text{ cm}^{-1}$ , i.e. to about 664  $m\mu$ <sup>22</sup>. In comparison, this is significantly smaller than the corresponding shift for acetone<sup>26</sup>, which amounts to about  $2000\text{ cm}^{-1}$ . (Strictly speaking, we ought to make our comparison with hexafluoroacetone.) This may be related to the fact that the  $n^*$  electrons in NO have some charge density both on the N and O atom, whereas in the keto-group the nonbonding electrons are practically exclusively located on oxygen. The change in charge distribution is thus very much larger in the  $n-\pi^*$  transition of the ketone, and the transition energy is more sensitive to the polarization of the surroundings. This may be part of an explanation, but probably not the complete one. We will continue to discuss this question in connection with the nitro group. It appears that perfluoronitrosoalkanes decompose by an excited molecule mechanism when they absorb visible light ( $n^*-\pi^*$ ), and by bond rupture, with probable formation of free NO, upon irradiation with ultraviolet radiation<sup>22</sup>.

Dimeric nitrosoalkanes have been isolated<sup>27</sup> and occur in *cis* and *trans* form. While the nitroso group contains  $2\pi$  electrons, the dimers



are to be considered as  $6\pi$  electron systems. The *trans* dimethyl dimer absorbs at 276  $m\mu$  in  $\text{H}_2\text{O}$  and 291  $m\mu$  in  $\text{CCl}_4$ , the *cis* compound at 265  $m\mu$  and 291  $m\mu$  respectively. This relatively strong band is ascribed to a  $\pi-\pi^*$  transition, its log  $\epsilon$ -value being always about 4. The absence of transitions at longer wave length, i.e. the disappearance of the  $n^*-\pi^*$  transition of the monomer, agrees with the assumed structure.

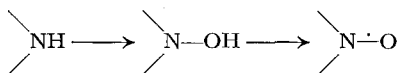
Calculated bond orders<sup>28</sup> for the N—N and N—O bonds have been compared to crystallographically determined values for the bond lengths, which are, for *cis* [CH<sub>3</sub>NO]<sub>2</sub>  $r_{\text{NN}} = 1.31 \text{ \AA}$ ,  $r_{\text{NO}} = 1.31 \text{ \AA}$ <sup>29</sup>, for *trans* [CH<sub>3</sub>NO]<sub>2</sub>  $r_{\text{NN}} = 1.22 \text{ \AA}$ ,  $r_{\text{NO}} = 1.25 \text{ \AA}$ <sup>30</sup> and for *trans* [(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>NO]<sub>2</sub>  $r_{\text{NN}} = 1.27 \text{ \AA}$ ,  $r_{\text{NO}} = 1.30 \text{ \AA}$ <sup>31</sup>. In the *trans* compound the N—N bond appears in general to be shorter.

The bond dipole moment for the N—O bond has been deduced to be about 2.0 D<sup>32</sup>. McEwen's molecular orbitals are not well suited to assess the dipole moment of nitrosomethane theoretically, as only part of the  $\sigma$  electrons are taken into account. An estimate of the contribution of the  $\pi$  electrons to the dipole moment gives between 1.2 D and 1.6 D in the sense  $\overset{+}{\text{N}}\overset{-}{\text{O}}$ , depending on which set of molecular  $\pi$  orbitals are used (reference 21 or reference 23).

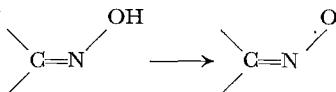
## B. Nitroxides and N-Oxides

### 1. Electronic and magnetic properties of nitroxide radicals

The paramagnetism of NO, which is dormant in the nitroso group, comes out very strikingly in nitroxides. Two types of nitroxide radicals are known and have been investigated, some that are derivable from amines, according to the general scheme



and others derivable from oximes



As the electronic structure of these two types is quite different, we will treat them separately.

*a. Nitroxides from amines.* Diphenylnitricoxide was first prepared in 1914<sup>33</sup>; some of its properties will be discussed in section III.C. Nitroxides derivable from aliphatic amines have also been known for a few years<sup>34-42</sup>, some of which are very stable. Until recently it was generally assumed that for an organic free radical to be stable its unpaired electron had to be highly delocalized, as is, for instance, the unpaired  $\pi$  electron in pentaphenylcyclopentadienyl. However, in stable aliphatic nitroxides the unpaired electron density is largely 'trapped' on the NO group, and is to a great extent prevented from spreading out over other parts of the molecule. According to Linnett<sup>43</sup>, the stability of these compounds towards dimerization (as

opposed to nitroso compounds!) is due to the fact that upon dimerization there is no net gain in the number of bonds formed (i.e. in the number of electrons participating in bonding). It should be for the same reason that the free molecule NO does not form the compound  $N_2O_2$ . Unquestionably the methyl groups in  $\alpha$  position to the nitroxy group also play a role in stabilizing the compounds

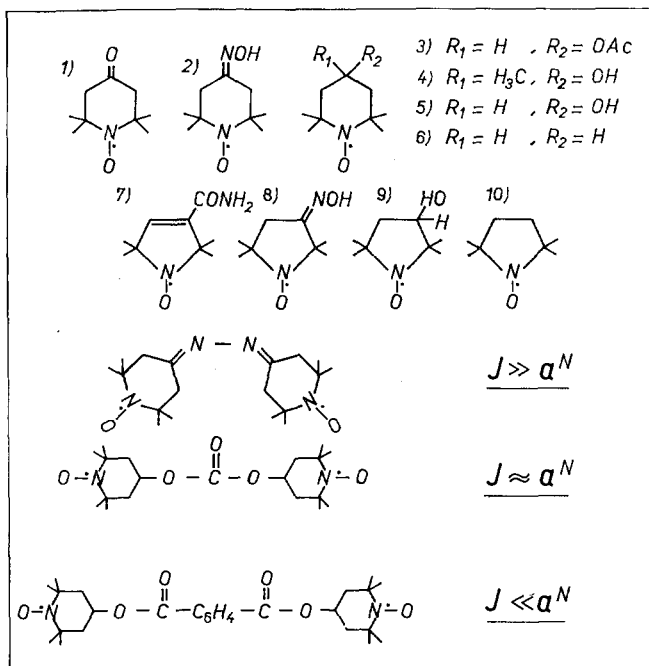


FIGURE 3. Stable nitroxide radicals, the properties of which are summarized in Table 4. The three biradicals shown represent the three cases of strong, intermediate and weak electron exchange.

shown in Figure 3. It is to be noted that the nitroxide radical derived from piperidine, for instance, is quite unstable<sup>42</sup>.

The nitroxy group is isoelectronic with the ketyl group. It may be written either as  $>\ddot{N}-\dot{O}$  or  $>\dot{N}-\ddot{O}$ . The first structure is apparently favored over the second one<sup>42</sup>. From the LCAO-MO point of view one may assume that it can be described by a similar set of molecular orbitals as a keto group, namely, a bonding orbital  $\pi$ , an antibonding orbital  $\pi^*$  and a nonbonding orbital  $n$  (mainly the  $2p_y$  orbital of the oxygen atom). The nitrogen atom appears to be

hybridized in a similar way as in the nitro group, or in pyrrole, and contributes two  $\pi$  electrons to the system, whereas only one  $\pi$  electron comes from oxygen, as in a ketone, and the nonbonding oxygen orbital contains two electrons. The unpaired electron is assumed to be located in the  $\pi^*$  orbital. This situation is visualized in Figure 4. From the point of view of the  $\pi$  electrons the N atom behaves as if it were more electronegative than the O atom. Such an

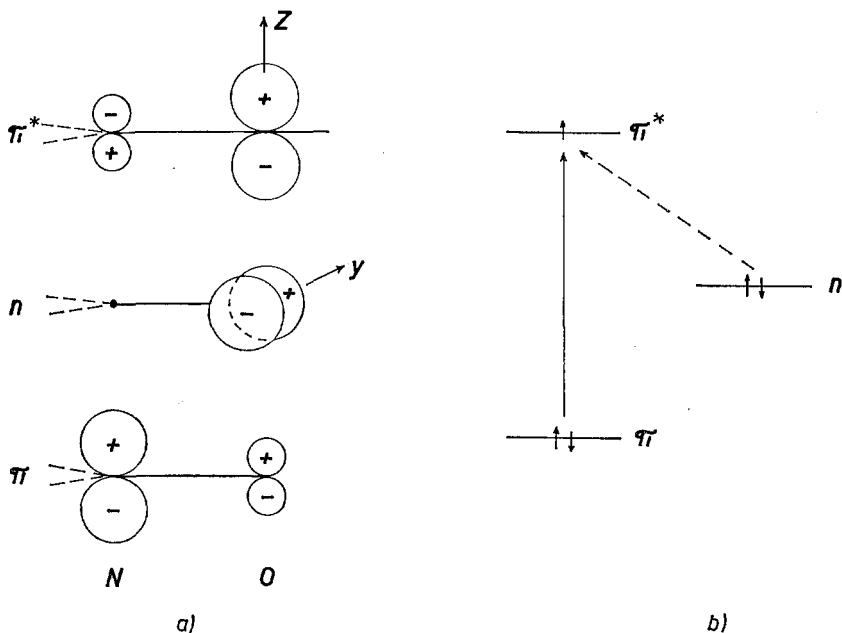


FIGURE 4(a). Simplified picture of the  $\pi$  orbitals and the nonbonding orbital of the N—O group in nitroxides derived from amines.

(b). Corresponding energy-level diagram.

electronic structure also agrees with the finding that these stable nitroxides are not basic.

The electronic structure and physical properties of a series of stable aliphatic nitroxide radicals were initially investigated mainly by American<sup>34,35</sup>, Russian<sup>41</sup> and French<sup>36,42,44</sup> research teams. As all radicals, they may be studied by electron spin resonance<sup>45</sup>. Of great interest is the hyperfine splitting due to the N<sup>14</sup> nuclear spin (see Figure 5), which has a value of 1. It can therefore couple in three different ways with the electron spin, corresponding to the values +1, 0, -1, splitting the ESR transition in a strong magnetic field into three separate lines of equal intensity. Each line in this

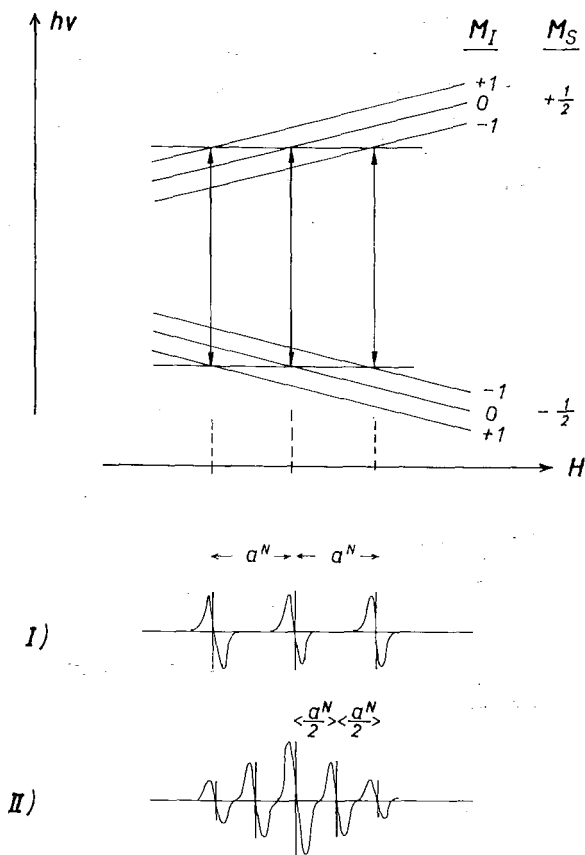


FIGURE 5. I. ESR hyperfine splitting pattern due to the interaction of an unpaired electron with a spin-1-nucleus ( $N^{14}$ ).

II. ESR hyperfine splitting pattern due to the interaction with two equivalent spin-1-nuclei. In the case of a biradical with strong electron exchange the separation of the lines is reduced to  $a^N/2$  (see reference 49).

triplet may be further split by the weaker interaction with the spin of  $\frac{1}{2}$  of the  $C^{13}$  atom of an adjacent methyl group<sup>36,46</sup>, and the even weaker splittings due to protons may also be observed in some cases<sup>35,42</sup>. In an actual spectrum one furthermore may encounter a weak doublet, separated by about 21 Gauss, arising from molecules containing  $N^{15}$  (spin of  $\frac{1}{2}$ ) in natural abundance (0.36%)<sup>42</sup>.

Values for the  $N^{14}$  splitting constants  $a^N$  for compounds 1-12 (Figures 3 and 5) are shown in Table 4, as well as values for  $a^C$ . From the theoretical interpretation of these values one ought to be



TABLE 4. ESR and UV spectral properties of some stable nitroxides. The data are from the following references: Compounds 1–10, references, 36, 42, and 44; Cpd. 11, reference 34; Cpd. 12, reference 35.

(i) Note the increase of  $a^N$  for decreasing polarity of the substituent at position 4 in the six-rings, at position 3 in the five-rings. (ii) Note that  $a^O$  is in general larger in the five-rings. A geometrical discussion of this fact may be found in reference 42. (iii) Note the blue shift of the  $n-\pi^*$  transition in going from nonpolar to polar solvents.

Compound (see Figure 3)	$a^N$	$a^O$	$\pi-\pi^{*c}$ $\lambda$ (m $\mu$ ) $\epsilon$	$n-\pi^{*b}$ $\lambda$ (m $\mu$ ) $\epsilon$	$n-\pi^{*c}$ $\lambda$ (m $\mu$ ) $\epsilon$
1	15.1 $\pm$ 0.1 <sup>a</sup>	5.6 $\pm$ 0.2 <sup>a</sup>	240	2610	450
2	15.4	5.5	240	2960	445
3	15.9		240	2012	472
4	15.9		240– 242	5400	445
5	16.0		239	1720	470
6	16.2		242– 247	1870	470
7	14.9	6.4	206 280	19500 1280	445
8	15.1	6.8	237	2800	430
9	15.2	6.8	233.5	2600	435
10	15.3	6.8	233	2500	435
11 Di- <i>t</i> -butyl- nitroxide	15.75 <sup>e</sup>				
12 Di- <i>n</i> -hexyl- nitroxide	16.4 <sup>b</sup>	$a^H(CH_2) =$ 11.0			

<sup>a</sup> Diethylene glycol.

<sup>b</sup> Cyclohexane, hexane or heptane.

<sup>c</sup> Methanol.

<sup>d</sup> Chloroform.

<sup>e</sup> Acetonitrile.

<sup>f</sup> Benzene.

able to make deductions about the electronic and overall structure of the molecule.

The hyperfine structure of ESR lines in solution is due to the Fermi contact interaction, which implies that there must be a finite unpaired electron density at the atomic nucleus in question. If, as we assume, the unpaired electron is in a  $\pi$  orbital, which has a node at the *N*-nucleus, the unpaired electron density at that nucleus vanishes, and one might expect the hyperfine coupling to be zero. As is well known, this is in general not the case. As long as we represent the ground state of the molecule by a single Slater determinant with all orbitals doubly occupied except the single-electron orbital, we must distinguish between the actual density of the unpaired electron  $\rho$  (given by  $\varphi^*\varphi$ ;  $\varphi$  being the orbital of the unpaired electron) on one hand, and the unpaired spin density on the other. The hyperfine interaction is of course determined by the

latter. McConnell and Chesnut<sup>47</sup> have shown how a lone electron in a  $\pi$  orbital may by an indirect coupling mechanism induce some unpaired spin density in a  $1s$  or  $2s$  orbital centered at a given nucleus, thereby leading to a contact interaction with that nuclear spin. This effect will, however, always be relatively small. Nevertheless, a simple relationship may often be found, relating the  $\pi$  density  $\rho_q^\pi$  of the unpaired electron on a given atom  $q$  with the hyperfine coupling constant (see also section III.B.2). Semiempirical calculations of type  $a$  (see section I.B) have been carried out on the system<sup>48</sup>

$\text{C} \rightarrow \text{N}-\text{O}$ , by which values for  $\rho_N^\pi$  were obtained.

Assuming the simple relation

$$a^N = Q^N \rho_N^\pi \quad (1)$$

where  $Q^N$  is a constant of proportionality, and taking an average value for  $a^N$  of 16.2 gauss,  $Q^N$  is found to be 59.3 gauss<sup>48</sup>. This value agrees reasonably well with similar findings for the nitromethane anion, where the unpaired electron also is located in a  $\pi$  orbital, as we shall see in section II.C.2.

It is also possible to form stable nitroxide diradicals<sup>49,50</sup>. This gives the means of estimating the extent of delocalization of the unpaired electrons. If the orbitals of the two unpaired electrons overlap, the electrons will interact, leading to a singlet state and a triplet state (direct dipole-dipole coupling may be assumed to be averaged out in liquid phase). The stronger the interaction between the two electrons,  $J$ , the more will the singlet state and the triplet state be split apart. We can now distinguish between two extreme cases. (a) If the interaction between the spin of a single electron and the N nucleus of the nitroxide group to which it belongs is much larger than the interaction between the two electrons,  $J \ll a^N$ , then each electron will only 'see its own' N nucleus and the ESR spectrum will be that of two independent radicals, showing, as before in the case of  $\text{N}^{14}$ , a triplet. (b) If, on the other hand, the coupling between the two unpaired electrons is significantly larger than the electron spin-nuclear spin coupling,  $J \gg a^N$ , then the unpaired electrons will 'see' both N nuclei and in the ESR spectrum a quintet will appear, with intensity ratio 1:2:3:2:1 and split by an interval of  $a^N/2$ . A quintet is the splitting pattern expected from two equivalent nuclear spins of 1. As  $a^N$  is very small (of the order of  $10^{-3}$  to  $10^{-2}$  cm<sup>-1</sup>), the situation (b) is already attained when the coupling between the two radical fragments is still imperceptible in

UV spectra<sup>50</sup>. Nitroxide diradicals enable one to study case (a), case (b) and various intermediate cases<sup>51</sup>. This is interesting, because due to the biradical paradox<sup>52</sup> case (a) appeared predominantly in many diradicals investigated previously<sup>53–55</sup>, in which the unpaired electrons are nonetheless highly delocalized, and in which MO-theory predicted  $J$  to be much larger than  $a^N$ .

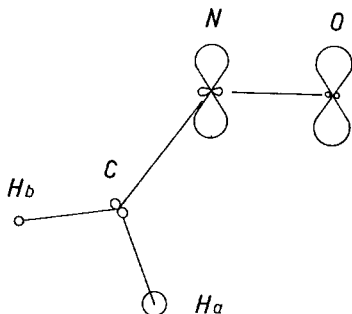


FIGURE 6. The density of the unpaired electron in the formaldiminoxy radical, as deduced theoretically in reference 48.

In the near ultraviolet spectrum<sup>42,44</sup> all compounds (except 7) show a band at about  $240 \text{ m}\mu$  ( $\epsilon \approx 3000$ ), in all likelihood attributable to an allowed  $\pi-\pi^*$  transition. In the visible there appears an absorption at about  $450 \text{ m}\mu$  ( $\epsilon \approx 5$ ), which may well be assigned to an  $n-\pi^*$  transition. Confirmation of this latter assignment may be found in the blue shift occurring in polar solvents, of the order of  $1300 \text{ cm}^{-1}$ , upon going from hexane to methanol. The similarity of the electronic structure of the nitroxy group with that of the keto group must be investigated further. In optically active, stable nitroxides of the type discussed here, one expects to find Cotton-effects at  $240 \text{ m}\mu$  and  $450 \text{ m}\mu$ . Such an optically active radical has indeed been synthesized<sup>56</sup>. The dependence of the relative sign and intensity of the  $450 \text{ m}\mu$  Cotton effect on the position of asymmetric substituents should obey similar sector rules as the  $300 \text{ m}\mu$  Cotton-effect in ketones<sup>57–59</sup>.

*b. Nitroxides from oximes.* Aliphatic iminoxy free radicals are less stable and have hitherto only been observed as transient species<sup>60,61</sup>. The salient fact about these radicals is that  $a^N$  is of the order of 30 gauss, thus twice as large as in aminoxides. This lends credence to the assumption that the unpaired electron is not located in a  $\pi$  orbital, but rather in an orbital of  $\sigma$  symmetry. As Berthier and

coworkers<sup>48</sup> show, the nitrogen splitting constant is now made up of two parts:

$$a^{\text{N}} = A^{\text{N}} \rho_{\text{N}}^{2s} + Q^{\text{N}} \rho_{\text{N}}^{2p} \quad (2)$$

$A^{\text{N}}$  is the constant for direct isotropic coupling between electron spin and nuclear spin and is taken to be 550 gauss<sup>62</sup>.  $Q^{\text{N}}$ , the constant of proportionality for indirect coupling, has already been discussed and a value of 59.3 gauss is deduced.  $\rho_{\text{N}}^{2s}$  represents the population of unpaired electron in the  $2s$  orbital of nitrogen,  $\rho_{\text{N}}^{2p}$  the population in those  $2p$  orbitals of nitrogen which do not belong to the  $\pi$ -system, namely  $\text{N}_x$  and  $\text{N}_y$ \*. Type- $a$  calculations on the fragment  $\text{N}=\text{O}$  give

C

the results shown in Table 5. One then deduces  $a^{\text{N}} = 31.1$  gauss, in

TABLE 5. Unpaired electron populations at the nitrogen atom in the fragment  $\text{C}=\text{N}-\text{O}$ , as calculated by Berthier and coworkers<sup>48</sup>.

$\rho_{\text{N}}^{2s}$	$\rho_{\text{N}}^{2p_x}$	$\rho_{\text{N}}^{2p_y}$
0.015	0.064	0.322

good agreement with experimental results. Though it is located in a  $\sigma$  orbital, Berthier and coworkers<sup>48</sup> find that most of the unpaired electron density nonetheless is still to be found on the  $\text{N}-\text{O}$  group.

## 2. The dative bond in trimethylamine $\text{N}$ -oxide

We have seen that the  $\text{C} \rightarrow \text{N}-\text{O}$  group, as encountered in nitroxides derived from amines, is paramagnetic and that it is not basic or

only weakly so. On the other hand,  $\text{N}$ -oxides of the type  $\text{C} \rightarrow \text{N}^+ \rightarrow \text{O}^-$

are diamagnetic, show a high degree of polarity and exhibit a strong tendency to form complexes with electron acceptors<sup>63,64</sup>. The semi-polar bond  $\text{N} \rightarrow \text{O}$  is customarily thought of as being formed by two  $\sigma$  electrons, which originally belong to the nitrogen atom, and

\* Our coordinate system is taken to coincide with Figure 6 and is not the one adopted in reference 48.

with which the oxygen atom seeks to fill its octet. The molecule  $(\text{CH}_3)_3\text{N}^+\text{O}^-$  shows a dipole moment of 5.02 D<sup>65</sup>. The length of the  $\text{N}^+ \rightarrow \text{O}^-$  bond has been determined as  $1.388 \pm 0.011 \text{ \AA}$  (values uncorrected for libration)<sup>66</sup>. The length of the  $\text{N}^+ \rightarrow \text{O}^-$  bond appears to increase upon complex formation. In  $(\text{CH}_3)_3\text{N}^+\text{O}^- \cdot \text{HCl}$  it grows to  $1.425 \text{ \AA}$ <sup>67,68</sup>.

The ultraviolet absorption spectrum of trimethylamine *N*-oxide<sup>69</sup> in acetonitrile solvent shows a band at about 198 m $\mu$  ( $\epsilon \approx 2350$ ). In ethyl alcohol and in water this band gets strongly shifted to the blue and decreases in intensity. Based on this fact and on intensity calculations, Kubota and coworkers<sup>69</sup> interpret this absorption as a degenerate  $n \rightarrow \sigma^*$  transition, corresponding to the excitation of a lone pair electron on the oxygen atom to the  $\sigma^*$  molecular orbital of the N—O bond. This orbital is taken as the antibonding linear combination of an  $sp^3$  hybrid orbital on the nitrogen atom and the  $2p_\sigma$  orbital of oxygen. The nonbonding orbital  $n$  is assumed to consist of either one of the almost degenerate  $2p_\pi$  orbitals of oxygen. The symmetry of these orbitals tells us immediately that the electric dipole transition must be polarized perpendicular to the bond axis.

## C. Nitrogen Dioxide and Nitroalkanes

### I. The electronic structure of NO<sub>2</sub>

*a. General discussion. The position of the unpaired electron.* Nitrogen dioxide is best treated theoretically in connection with its positive and negative ions. Data on the geometry of these molecules may be found in Table 6.

TABLE 6. Bond lengths and angles in nitrogen dioxide and its ions.

	$\text{NO}_2^+$ <sup>a</sup>	$\text{NO}_2$ <sup>b</sup>	$\text{NO}_2^-$ <sup>c</sup>
$r_{\text{NO}}(\text{\AA})$	1.153	1.1934	1.236
$\angle \text{ONO}$	180°	134.07°	115.4°

<sup>a</sup> Reference 72. <sup>b</sup> Reference 71. <sup>c</sup> Reference 70.

Walsh has investigated in a general way the molecular orbitals, shapes, and spectra of different types of smaller molecules and in particular also of the type AB<sub>2</sub><sup>73</sup>. On symmetry grounds and by

semiquantitative arguments concerning the energy he has plotted a diagram correlating the orbitals of triatomic molecules of this kind as a function of the angle  $\angle BAB$ , going from  $90^\circ$  to  $180^\circ$ . This implies a change from symmetry  $C_{2v}$  to symmetry  $D_{\infty h}$  and enables him to make the following predictions concerning the geometry: 'Molecules with no more than 16 valence electrons are linear in their ground states; molecules with 17, 18, 19 or 20 valence electrons are bent in their ground states, the apex angle decreasing markedly

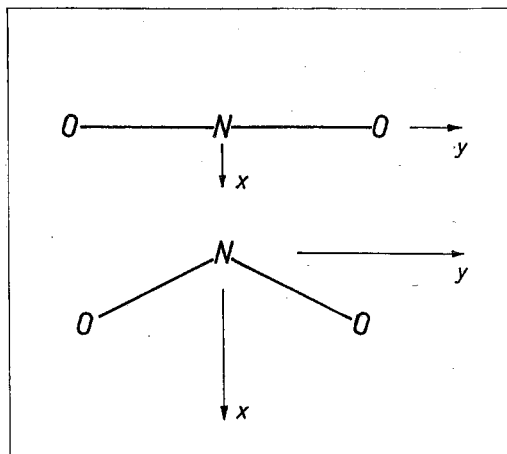


FIGURE 7. Cartesian coordinates, as adopted for the description of  $\text{NO}_2^+$  and  $\text{NO}_2$ .

from 16- to 17- and from 17- to 18-electron molecules . . .'. These predictions are well confirmed experimentally in the case of  $\text{NO}_2$ . General investigations of this kind have also been carried out by Mulliken<sup>74, 75</sup>.

Recently a number of semiempirical calculations on  $\text{NO}_2$  have appeared in the literature, using different methods of approach: McEwen's<sup>76</sup> calculation is of type *a* (see section I.B.), although the  $\sigma$  electrons are taken into account only in a limited way. Fukui and coworkers<sup>77</sup> apply the extended Hückel treatment (type *c*) to  $\text{NO}_2$  and its ions. Different authors have investigated the relative role<sup>78-84</sup> played by  $\pi$  and  $\sigma$  electrons in the formation of the dimer  $\text{N}_2\text{O}_4$ . The method of 'nonpaired spatial orbitals', applied to the  $\pi$  electrons of  $\text{NO}_2^+$ ,  $\text{NO}_2$  and  $\text{NO}_2^-$ , has been compared to valence bond and molecular orbital calculations<sup>85</sup>. Unfortunately, *ab initio* calculations on  $\text{NO}_2$  may not as yet be found in the literature. There exists a

calculation of this type by Clementi and McLean<sup>86</sup> on the iso-electronic ions NO<sub>2</sub><sup>+</sup> and N<sub>3</sub><sup>-</sup>, both of which are linear and symmetrical.

It appears to be very important to consider both the  $\sigma$  and the  $\pi$  electrons to gain a deeper understanding of the electronic structure of NO<sub>2</sub>. For this reason we compare in somewhat more detail the molecular orbitals for NO<sub>2</sub> obtained by McEwen and by Fukui.

In both calculations molecular orbitals are written as linear combinations of the  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$  atomic orbitals of the nitrogen and the oxygen atoms. In both calculations molecular orbitals for the lower electrons are not given explicitly. The three lowest molecular orbitals are of course built mainly from the  $1s$  functions of oxygen and nitrogen and contain the six inner shell electrons. Then follow the orbitals of the actual valence electrons, of which the three lower ones are not shown here either. They correspond to the orbitals designated by  $s_1$ ,  $s_2$  and  $\sigma_g-a_1'$  in Walsh's notation<sup>73</sup>.

The correlations of the next seven orbitals, as calculated by Fukui and coworkers, for bent NO<sub>2</sub> and linear NO<sub>2</sub><sup>+</sup> are represented in Figure 8. The lowest empty orbitals of NO<sub>2</sub><sup>+</sup>, labelled  $\pi_u^*$ , of symmetry  $e_{1u}$ , split into a  $\pi$  orbital of symmetry  $b_1$  and a  $\sigma$  orbital of symmetry  $a_1$  in the bent molecule. The latter  $a_1$  orbital is very sensitive to the bond angle  $\angle$ ONO and gets drastically pushed down as the angle decreases. NO<sub>2</sub><sup>-</sup> is stabilized by making the angle even smaller. It is this  $\sigma$  orbital which apparently contains the unpaired electron in NO<sub>2</sub>, but contains an electron-pair in NO<sub>2</sub><sup>-</sup>. We then also conclude that there are  $4\pi$  electrons in NO<sub>2</sub>, two of which must come from the nitrogen atom, which accordingly is in the same valence state as, for instance, in pyrrole.

There is agreement between Fukui's and McEwen's results concerning the orbital of the unpaired electron. However, the energetic sequence of some orbitals is somewhat different. This is due to significant differences in the method of calculation.

On the question of whether the unpaired electron in NO<sub>2</sub> is located in a  $\sigma$  or a  $\pi$  orbital some divergent views are also found in the literature<sup>81, 85</sup>.

*b. Electron interaction and ionization potentials*<sup>†</sup>. Fukui uses the extended Hückel method<sup>8</sup> and seeks the solutions of the secular determinant

$$\det |H_{qr} - eS_{qr}| = 0, \quad (2)$$

where the diagonal elements of the effective Hamiltonian  $H$  are

<sup>†</sup> The less theoretically inclined reader may skip the major part of this subsection.

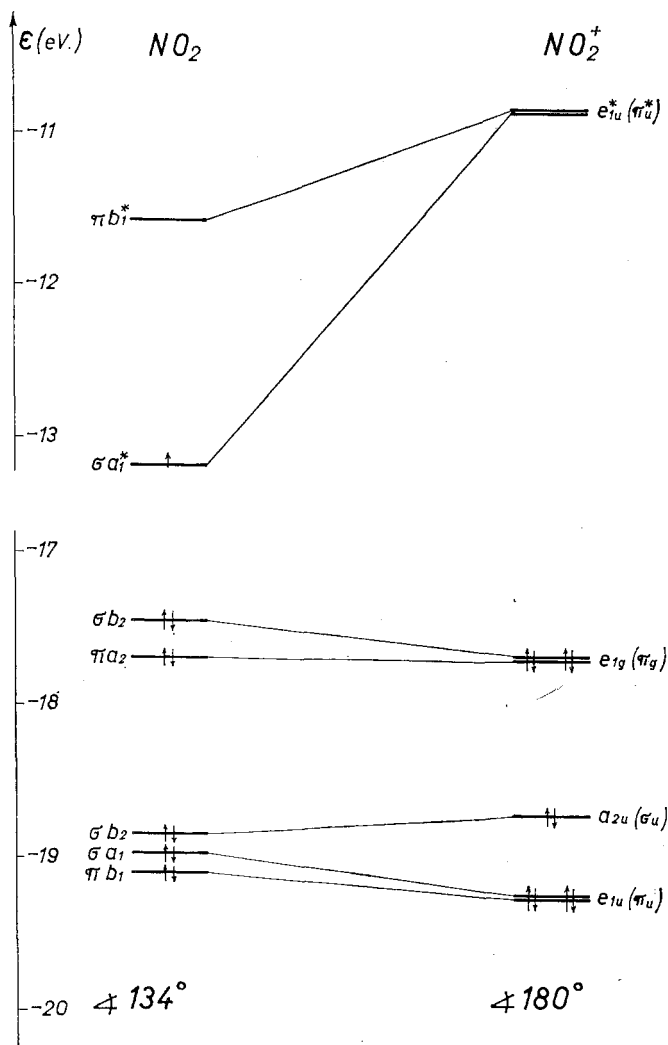


FIGURE 8. The correlation of the orbitals of  $\text{NO}_2^+$  and  $\text{NO}_2$  as calculated in reference 77.

taken as the first ionization potentials of the atoms in the respective valence states<sup>87,88</sup>:  $H(2s, N) = -27.5$  eV,  $H(2p, N) = -14.5$  eV,  $H(2s, O) = -35.3$  eV,  $H(2p, O) = -17.8$  eV and off-diagonal elements are calculated from the formula  $H_{qr} = 0.5K(H_{qq} + H_{rr})S_{qr}$ , where  $K$  is an adjustable parameter, taken to be 1.75.  $H_{qq}$  and  $H_{rr}$  are the diagonal elements of orbitals  $q$  and  $r$  and  $S_{qr}$  the overlap integral between these orbitals. Electron interaction is not taken into account explicitly in these calculations.



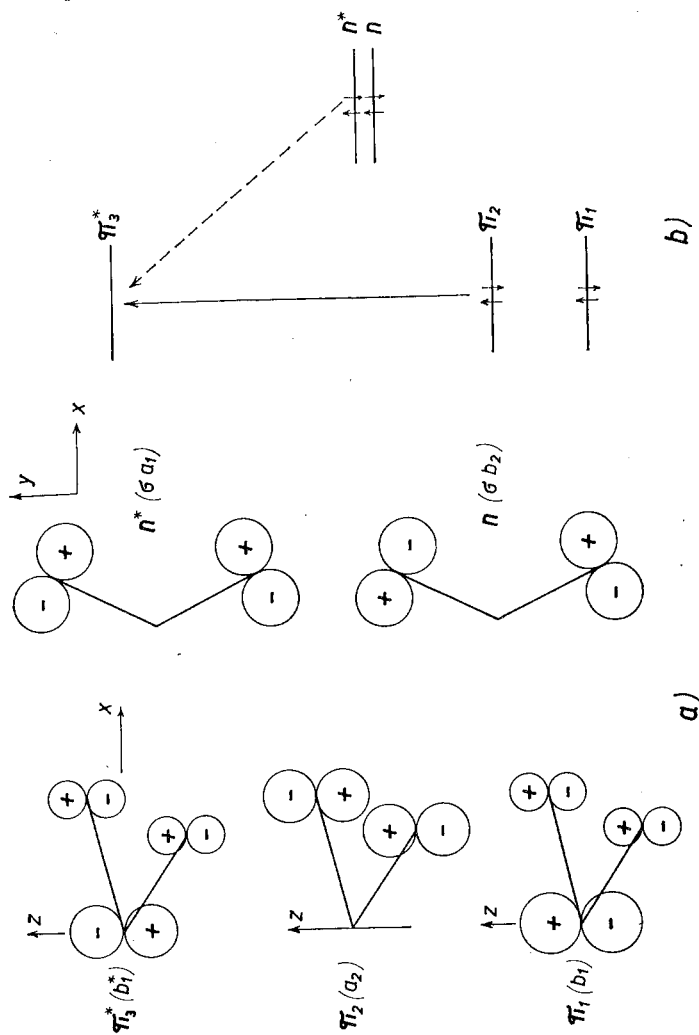


FIGURE 9. Simplified picture of the  $\pi$  and nonbonding orbitals of the nitro group, as it may be applied to nitromethane. The relative energy of the nonbonding orbitals is the one deduced by McEwen<sup>76</sup>. The detailed numerical form of these orbitals is given in Table 10. McEwen's calculations show the antisymmetric nonbonding orbital to lie below the symmetric one by 0.04 eV.

On the other hand, McEwen is interested in the solutions of the SCF secular determinant of the type:

$$\det |F_{qr} - \epsilon S_{qr}| = 0. \quad (3)$$

The Fock operator  $F$  consists of three terms\*:

$$F = h + 2J - K; \quad (4)$$

$h$  represents the kinetic energy of an electron and its electrostatic interaction with the atomic cores.  $J$  contains the electrostatic repulsions with the other electrons and  $K$  the exchange interactions. Written in this way the SCF equation may only be applied to closed-shell systems, i.e. systems containing an equal number of electrons with spin  $\alpha$  and spin  $\beta$ , distributed pairwise in the orbitals of lowest  $\epsilon$  value. These equations imply that electrons with spin  $\alpha$  and electrons with spin  $\beta$  may be treated in an equivalent way. While the electron repulsion terms (Coulomb terms) are spin-independent, the exchange terms are not. Now  $\text{NO}_2$  is not a closed shell system, but a radical. The number of spin- $\alpha$  electrons is not equal to the number of spin- $\beta$  electrons and the exchange effects on an electron will be different according to its spin-state. To take this into account, one will end up by having two distinct sets of equations, one set for the  $\alpha$ -electrons, another set for  $\beta$ -electrons, leading to different orbitals for electrons of different spin<sup>89</sup>. However, if this is carried out rigorously the ground state of the molecule may no longer be written as a single Slater determinant, as such a single determinant does not correspond to a definite spin-value for the molecule as a whole. This complicates the problem significantly, and one must then use particular open-shell SCF procedures, the details of which may be found in the literature<sup>90-94</sup>.

According to McEwen's calculations it appears that differences between orbitals occupied by spin- $\alpha$  electrons and orbitals occupied by spin- $\beta$  electrons are small in the case of the  $\pi$  and the bonding  $\sigma$  orbitals. Only for the nonbonding  $\sigma$  orbital of symmetry  $b_2$  does the energy-difference become more important—depending on the presence or absence of exchange effects with the unpaired electron (see Table 7)—but the spatial part of the orbital remains little affected. To a good approximation the ground state may still be expressed as a single Slater determinant of doubly occupied spatial orbitals, plus one impaired electron.

\*  $J$  stands for  $\sum_i J_i$ ,  $K$  for  $\sum_i K_i$ , where  $J_i$  and  $K_i$  are Coulomb and exchange operators associated with the molecular orbital  $\varphi_i$ , as defined in reference 5. The summation is carried over the (doubly) occupied orbitals.

TABLE 7a. LCAO-coefficients for MO's of NO<sub>2</sub> as given by Fukui and coworkers, reference 77.

Symmetry	$\epsilon_i$	$n_i$	$N_s$	$N_x$	$N_y$	$O_s$	$O'_s$	$O_x$	$O'_x$	$O_y$	$O'_y$	$N_z$	$O_z$	$O'_z$
$\pi b_1^*$	-11.58											0.949	-0.454	-0.454
$\sigma a_1^*$	-13.19	1	0.319	-0.802		-0.022	-0.022	0.487	0.487	-0.037	0.037			
$\sigma b_2$	-17.46	2			-0.061	-0.005	0.005	0.537	-0.537	0.472	0.472			
$\pi a_2$	-17.69	2												
$\sigma b_2$	-18.85	2			0.275	0.131	-0.131	0.416	-0.416	-0.426	-0.426		0.710	-0.710
$\sigma a_1$	-18.98	2			0.368	-0.061	-0.061	0.461	0.461	0.366	-0.366			
$\pi b_1$	-19.11	2										0.414	0.570	0.570

 $\epsilon_i$  designates the energy of the orbital, and  $n_i$  the occupancy.TABLE 7b. LCAO-coefficients for MO's of NO<sub>2</sub> as given by McEwen, reference 76.

	$\epsilon_i$	$n_i$	$N_s$	$N_x$	$N_y$	$O_s$	$O'_s$	$O_x$	$O'_x$	$O_y$	$O'_y$	$N_z$	$O_z$	$O'_z$
$\pi b_1^*$	-2.23											0.798	-0.426	-0.426
$\sigma a_1^*$	-14.09	1	0.314	-0.513		0.007	0.007	0.556	0.556	-0.080	0.080			
$\beta$	-12.89	2	{	{	0.020	-0.007	0.007	0.683	-0.683	0.181	0.181			
	-16.90				-0.020	0.007	-0.007	0.683	-0.683	0.181	0.181			
$\alpha$	-15.85	2												
$\pi a_2$	-19.98	2												
$\pi b_1$	-19.98	2												
$\sigma a_1$	-20.33	2	-0.256	0.639		0.000	0.000	0.412	0.412	0.312	-0.312	0.603	0.707	-0.707
$\sigma b_2$		2											0.564	0.564

The orbitals have been transformed to the coordinate system adopted by Fukui and coworkers<sup>77</sup> (see Figure 7).



This being the case, the energy-eigenvalue of the highest occupied molecular orbital is still assumed to give an acceptable approximation to the first ionization potential. Now, a question arises however: does this first ionization potential correspond to the subtraction of the unpaired electron from the orbital  $a_1^*$ —which one would expect on intuitive grounds—or of the electron with  $\beta$ -spin from the orbital  $b_2$ , leaving behind two unpaired electrons of spin  $\alpha$ , namely, an ion in a triplet state? This question can only be answered by invoking configuration interaction. The first calculated ionization potential is found to be 13.21 eV and leads to a state which may be represented as a superposition of two configurations. The dominant configuration corresponds to a subtraction of the unpaired electron from  $a_1^*$ ; but there is also a significant contribution from a singlet configuration in which the  $b_2$ -orbital is empty and the  $a_1^*$ -orbital doubly filled, corresponding to a subtraction of one  $b_2$ -electron and subsequent pairing of two electrons in  $a_1^*$ .

At the level of approximation adopted by Fukui and coworkers the first ionization potential is simply given by minus the energy of  $-13.19$  eV of the orbital occupied by the unpaired electron. In view of the great difference of approach the agreement with McEwen's result is perhaps somewhat fortuitous. Furthermore, the correlation with experimental data is not unambiguous. The observed ionization potentials of nitrogen dioxide are the following: (a) 9.9 eV, estimated by Kandel<sup>95</sup>, (b) a value  $>11.7$  eV, assessed by a photo-ionization technique<sup>96</sup>, (c) 12.3 eV, from a Rydberg series<sup>97</sup>, and (d) 13.98 eV, detected by electron impact<sup>98</sup>. It is the first vertical ionization energy which has to be compared to the theoretical value given above. McEwen assumes the value  $\sim 11.7$  eV to be closest to such a situation. Consequently, the calculated ionization potential appears to be too high.

The electronic spectrum of NO<sub>2</sub> consists of extensive absorptions in the visible, between  $910\text{ m}\mu$  and  $320\text{ m}\mu$ , in the near ultraviolet, mainly between  $260\text{ m}\mu$  and  $200\text{ m}\mu$ , and in the vacuum ultraviolet, between  $160\text{ m}\mu$  and  $135\text{ m}\mu$ <sup>77</sup>. The transitions in the visible probably mainly correspond to low-energy single excitations to or from the lone-electron orbital  $a_1^*$ . These long-wavelength bands disappear in nitro compounds. Detailed assignments of the NO<sub>2</sub> spectrum remains tentative however and open to discussion<sup>76, 77</sup>.

The density of the unpaired electron at the nitrogen nucleus may be estimated from the isotropic hyperfine splitting in the ESR spectrum. For NO<sub>2</sub> in CCl<sub>4</sub> solution  $a^N$  has been measured to be

108 gauss<sup>99</sup>. Assuming for simplicity this splitting to be entirely due to direct coupling

$$a^N = A^N \cdot \rho_N^{2s}, \text{ and taking } A^N = 550 \text{ gauss} \quad (5)$$

(as in section II.B.1.b), leads to an unpaired electron density in the  $N_s$  (nitrogen  $2s$ ) orbital  $\rho_N^{2s}$  of 0.196. (G. R. Bird and coworkers<sup>99</sup> deduce  $\rho_N^{2s} = 0.18$ ). An MO calculation by Green and Linnett<sup>84</sup> leads to  $\rho_N^{2s} = 0.168$ .

Measurements of the ESR spectrum in solid phases all lead to a smaller value for the isotropic hyperfine coupling constant, of between 50 and 60 gauss<sup>100</sup>. This appears to agree better with the value of  $\rho_N^{2s}$  of about 0.10, as obtained by McEwen. This latter result is also in agreement with the value for  $\rho_N^{2s}$  deduced from the hyperfine structure of the rotational spectrum<sup>71,101</sup>.

Measurement of the dipole moment of  $N^{15}O_2$ <sup>16</sup> by the microwave Stark effect yields a value of 0.29 D<sup>102</sup>.

## 2. The electronic properties of nitroalkanes

Electron diffraction studies on nitromethane were already carried out in 1935<sup>103</sup>. Further measurements<sup>104</sup> were performed on  $CF_3NO_2$  and  $CBr_3NO_2$ , the results being shown in Table 9. Nitromethane has a sixfold barrier to internal rotation  $V_6$ , which however is extremely low<sup>105,106</sup>. Thus, the molecule may be considered to have an effective symmetry of  $C_{2v}$ , as the molecule  $NO_2$ . Values for the dipole moment  $\vec{\mu}_e$  have been obtained from the microwave Stark effect<sup>105,106</sup>.

TABLE 9. Structural data on nitromethane and related compounds

	$r_{CN}(\text{\AA})$	$r_{NO}(\text{\AA})$	$\angle ONO$	$V_6$ (cal/mole)	$\vec{\mu}_e(D)$
$CH_3NO_2$	1.46 <sup>a</sup>	1.21 <sup>a</sup>	127 <sup>a</sup>	$6.03 \pm 0.03^c$	$3.46 \pm 0.02^c$
$CF_3NO_2$	1.56 <sup>b</sup>	1.21 <sup>b</sup>	132 <sup>b</sup>	$74.4 \pm 5^d$	$1.44 \pm 0.03^d$
$CBr_3NO_2$	1.59 <sup>b</sup>	1.22 <sup>b</sup>	134 <sup>b</sup>		

<sup>a</sup> Reference 103, <sup>b</sup> reference 104, <sup>c</sup> reference 105, <sup>d</sup> reference 106.

The electronic structure of nitromethane has been studied by McEwen<sup>76</sup> and by Tanaka<sup>107</sup>. McEwen's results are shown in Table 10. These calculations are of the same order of approximation as the ones discussed for  $NO_2$  (see Table 7). Only the three  $\pi$  orbitals and the two nonbonding  $\sigma$  orbitals of symmetry  $b_2$  and  $a_1$  are determined explicitly.

It is striking that the two nonbonding molecular orbitals appear to be nearly degenerate and that they consist almost exclusively of

TABLE 10. LCAO-coefficients for  $\pi$  and nonbonding  $\sigma$  MO's of nitromethane according to McEwen<sup>76</sup>

Symmetry	$\epsilon_i$	$n_i$	C	N <sub>s</sub>	N <sub>x</sub>	N <sub>y</sub>	O <sub>s</sub>	O <sub>s</sub> '	O <sub>x</sub>	O <sub>x</sub> '	O <sub>y</sub>	O <sub>y</sub> '	N <sub>z</sub>	O <sub>z</sub>	O <sub>z</sub> '
$\pi b_1^*$	-3.61												0.684	-0.515	-0.515
$\pi a_2$	-15.51	2												0.707	-0.707
$\sigma a_1$	-16.11	2	0.240	-0.010	-0.020		0.010	0.010	0.674	0.674	0.132	-0.132			
$\sigma b_2$	-16.16	2				-0.010	0.004	-0.004	0.683	-0.683	0.182	0.182			
$\pi b_1$	-21.76	2											0.729	0.484	0.484

\* The coordinate system is chosen, as shown in Figure 7.

oxygen  $2p_x$  and  $2p_y$  functions. The  $a_1$  molecular orbital contains a small contribution of atomic  $2s$  and  $2p_x$  functions of carbon, collectively designated by  $C$ . The coefficients for the atomic orbitals of nitrogen appear, surprisingly, to be negligible. From the orbital energies one would expect the ionization potential for  $\text{CH}_3\text{NO}_2$  to be 15.51 eV, corresponding to the subtraction of an electron from the  $\pi a_2$  orbital. Experimentally one finds 11.34 eV<sup>95</sup>. The absolute value of the orbital energies is thus to be considered with caution. On the other hand, the transition energies of the electronic spectrum may be calculated to a first approximation from the relative differences of the SCF molecular orbital energies and from electron interaction terms<sup>5</sup>. For a singlet-singlet transition in which an electron is excited from an occupied orbital  $i$  to an empty orbital  $a$  the energy is given by the relation:

$$\Delta E_{ia} = \varepsilon_a - \varepsilon_i - J_{ia} + 2K_{ia} \quad (6)$$

where the Coulomb integral is expressed as

$$J_{ia} \equiv \int \varphi_i^*(1) \varphi_a^*(2) \frac{e^2}{r_{12}} \varphi_i(1) \varphi_a(2) d\tau$$

and the exchange integral

$$K_{ia} \equiv \int \varphi_i^*(1) \varphi_a^*(2) \frac{e^2}{r_{12}} \varphi_i(2) \varphi_a(1) d\tau.$$

The electronic spectrum of nitromethane is much simpler than that of  $\text{NO}_2$ . The complicated band system in the visible is absent, and the near-UV spectrum permits assignments with reasonable certainty. A weak band at 270  $m\mu$  has been extensively studied by several authors<sup>108-113</sup> and appears to arise from an  $n-\pi^*$  transition. More recently, Nagakura<sup>114</sup> has confirmed the existence of a band at 198  $m\mu$  in the gaseous state, with a maximum extinction coefficient of about 5000, which he attributes to a  $\pi-\pi^*$  transition<sup>115</sup>. This coincides quite well with McEwen's predictions, as shown in Table 11.

The blue shift of the  $n-\pi^*$  band of nitroparaffins in polar solvents is relatively small<sup>112</sup>. Going from solvents hexane to methanol, this blue shift in nitromethane is only of the order of 450  $\text{cm}^{-1}$  and consequently comparable to the one observed in nitrosoalkanes.

If electron donating groups are attached directly to the  $\text{NO}_2$ -group, the  $n-\pi^*$  transition gets shifted only insignificantly, in contrast to the huge shifts observed in corresponding nitroso compounds<sup>116,117</sup>. This is probably due to the fact that in nitroso compounds the



TABLE 11. Observed and calculated electronic transitions in nitromethane

Transition	$\lambda(\text{m}\mu)^a$	$f \text{ calc.}^a$	$\lambda(\text{m}\mu)^b$	$f \text{ obs.}^b$
	calc.		obs.	
$\pi-\pi^*$	214	0.33	198	$\sim 0.15$
$n-\pi^*$	272	0.0001	270	0.0004
$n^*-\pi^*$	281			

<sup>a</sup> Reference 76, <sup>b</sup> reference 113–115.

nonbonding orbital contains both contributions from the oxygen and the nitrogen atomic functions, whereas in nitro compounds the corresponding nonbonding electrons are almost exclusively located on the oxygens.

Of particular interest are the pseudo-acid properties of aliphatic nitro compounds in basic medium:



and the concomitant changes in spectral behavior<sup>114</sup>. By gradually changing the pH of an aqueous solution from 7 to 12, that is, by going from pure water to 0.01 *N* NaOH or KOH, the 270 *m* $\mu$  band becomes blurred, and a strong band gradually appears at 233 *m* $\mu$ , which may with good certainty be ascribed to the anionic form. From the change of the absorption curves with increasing pH value the acid dissociation constant (*pK<sub>a</sub>*) was determined as 10.1 at 25°, in reasonable agreement with the value measured electrometrically, 10.21 at 25°<sup>114</sup>.

Nitramide, which is isoelectronic with the nitromethane anion, exhibits a band at 225 *m* $\mu$  in water, which has been ascribed to an intramolecular charge-transfer transition from the NH<sub>2</sub> group to the NO<sub>2</sub> group<sup>118</sup>. Probably the 233 *m* $\mu$  band of the nitromethane anion may be interpreted similarly. A second possible assignment is that this band is a shifted 198 *m* $\mu$  absorption of the nitro group. This, however, is more unlikely, for the general effect of an electron donating substituent attached to a nitro group is to shift the nitro  $\pi-\pi^*$  transition to the blue. Nagakura<sup>114</sup> has also investigated the coupling between the two subsystems CH<sub>2</sub><sup>−</sup> and NO<sub>2</sub> theoretically, by considering the interaction of four configurations: a ground configuration *G*, a charge transfer configuration *CT* and two locally excited configurations *LE* and *LE'* (see Figure 10). From this calculation the first electronically allowed transition is

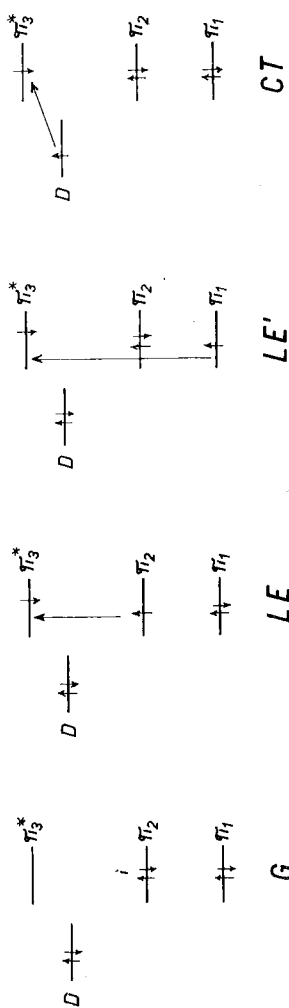


FIGURE 10. Ground, locally excited, and charge transfer configurations of the  $\pi$  electron system of a nitro group interacting with an electron donor (D).

predicted to occur at 208 m $\mu$  and to be predominantly of the charge-transfer type, while the next transition occurs only at 136 m $\mu$  and consists mainly of local excitation within the NO<sub>2</sub> group. Qualitatively this sequence supports the hypothesis that the 233 m $\mu$  absorption in the aci-form of nitromethane is the charge transfer band, and that the original 198 m $\mu$  absorption has been shifted drastically to the blue. However, only an extension of spectral measurements to shorter wavelengths can settle this question unambiguously.

Nitropropene shows an absorption at 229 m $\mu$  with a value for  $\epsilon_{\max}$  of 8700 in *n*-hexane. This band may also be assumed to contain a definite charge transfer contribution.<sup>118</sup>

The optical rotatory dispersion of a series of aliphatic nitro compounds has recently been studied, in particular of some nitro steroids<sup>119,120</sup>. In general, a strong Cotton effect is encountered in the 270–290 m $\mu$  region which may well be attributed to the  $n\rightarrow\pi^*$  transition, at least in cases where the nitro group is unconjugated with any double bond. Of special interest is the appearance, even in some saturated or unconjugated nitro steroids, of a weak band around 350 m $\mu$ , which must be associated with the nitro group. Such a band has hitherto not been reported for nitroalkanes. Its interpretation might be rather difficult.

The apparent lifetime of radical anions of aliphatic nitro compounds is of the order of 0.5 sec in aqueous solution at room temperature. These radicals are thus considerably less stable than their aromatic counterparts, but in general of sufficient stability to take well-resolved ESR spectra and to permit definite assignments<sup>121</sup>. Unfortunately nitromethane appears to be an exception, as no clear spectrum seems to have been obtained of this compound. In general, the strongest hyperfine splitting arises from the isotropic interaction of the unpaired electron spin with the N<sup>14</sup> nuclear spin. Further couplings are due to protons close to the nitro group. In compounds of the type R—CH<sub>2</sub>—NO<sub>2</sub> the strong N<sup>14</sup> triplet is thus split by the two equivalent protons at the C-atom adjacent to the nitro group into a further triplet. For instance, in CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> one finds  $a^N = 25.5$  gauss and  $a^H(\text{CH}_2) = 9.75$  gauss<sup>121</sup>. One may assume that the unpaired electron goes into the  $\pi b_1^*$  orbital (see Table 10) of the nitro group, although—in comparison with nitroxides— $a^N$  seems a bit large for an electron in a practically pure  $\pi$  orbital. But this assumption is supported by evidence from nitrobenzene anion radicals, as we shall see in section III.B.2. However, it is of

interest, that there exists a relatively large solvent effect on the  $N^{14}$  coupling constant for aromatic nitro compounds, whereas it is absent in the spectra of aliphatic compounds. The anion radical  $[R-CH_2-NO_2]^-$  must of course not be mistaken for the anion of the aci-form  $[R-CH=NO_2]^-$  which does not contain any unpaired electron.

TABLE 12. Proton chemical shifts in nitroalkanes

	$CH_4$	$CH_3NO_2$	$CH_2(NO_2)_2$	$CH(NO_2)_3$
$\tau$ p.p.m. <sup>a</sup>	9.767	5.72	3.90	2.48
	$CH_3NO_2$	$CH_3CH_2NO_2$	$CH_3(CH_2)_2NO_2$	$CH_3(CH_2)_3NO_2$
$\tau(CH_3)$ p.p.m. <sup>b</sup>	5.72	8.52	8.97	9.00

<sup>a</sup> Reference 122, <sup>b</sup> reference 123.

In the proton magnetic resonance spectra of nitroalkanes the local diamagnetic deshielding by the inductive effect of the nitro group is clearly exhibited<sup>122,123</sup>. Table 12 shows the cumulative influence of nitro groups bonded to one carbon atom and the long-range effect of one nitro group along a hydrocarbon chain. The anisotropic shielding effects of the nitro group on adjacent protons have also been studied and may be interpreted similarly to comparable effects in the carbonyl group, for instance<sup>124</sup> (see Figure 11).

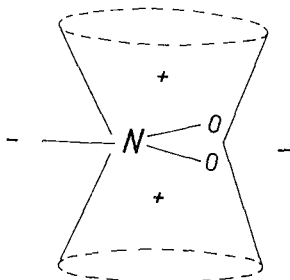


FIGURE 11. Qualitative description of the anisotropic NMR shielding effect of the nitro group, as discussed in reference 124.

### 3. On the structure of nitroethylene

The spectroscopic properties of nitroethylene have recently been investigated by Günthard and coworkers<sup>125,126</sup>. Microwave studies show that nitroethylene has a planar molecular structure. From the Stark effect the dipole moment has been measured to  $3.70 \pm 0.03$  D. The C—N bond length is found to be 1.470 Å, the N—O bond length

1.218 Å. From infrared measurements the barrier to internal rotation of the nitrogroup has been calculated to be  $6510 \pm 280$  cal/mole.

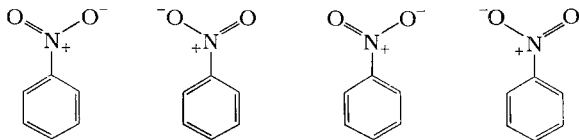
The near-ultraviolet spectrum of nitroethylene<sup>126</sup> shows bands at  $205 \text{ m}\mu$  ( $\epsilon \approx 11,000$ ),  $240 \text{ m}\mu$  ( $\epsilon \approx 2300$ ) and  $305 \text{ m}\mu$  ( $\epsilon \approx 50$ ). The first-mentioned band is interpreted as a transition predominantly localized within the nitro group and consequently related to the  $198 \text{ m}\mu$  absorption in nitromethane. The second band may be considered as a charge transfer transition from the ethylenic double bond to the nitro group<sup>126</sup>. Finally, the  $305 \text{ m}\mu$  absorption has in all likelihood  $n-\pi^*$  character. The spectra of 1-nitro-1-propene and 2-nitro-1-propene strongly resemble the one recorded for nitroethylene. On the other hand, in 3-nitro-1-propene steric inhibition to resonance between the nitro group and the ethylenic double bond occurs. In the near UV region the spectrum rather resembles that of nitromethane.

### III. AROMATIC C—NO AND C—NO<sub>2</sub> COMPOUNDS

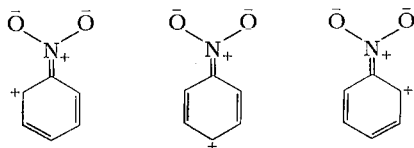
#### A. Ground and Excited State Properties of Nitrobenzene, Nitrosobenzene, and Their Derivatives

##### I. The electronic structure of nitrobenzene

X-ray measurements show the nitrobenzene molecule to be completely planar. Resonance theory<sup>127</sup> pictures nitrobenzene as a superposition of four Kekulé structures:



and of three ionic structures:



Assuming a significant influence of these ionic structures, one predicts that the N—O bond should be longer than in nitroalkanes,

the C—N bond shorter; the C—C bonds in the benzene ring should be unequal in length, the 1—2 bond being longest, the 2—3 bond shortest. These geometric predictions are however not substantiated by crystallographic data<sup>128</sup> (see Figure 12). The C—N bond length is, interestingly, rather longer than in nitromethane and the 2—3

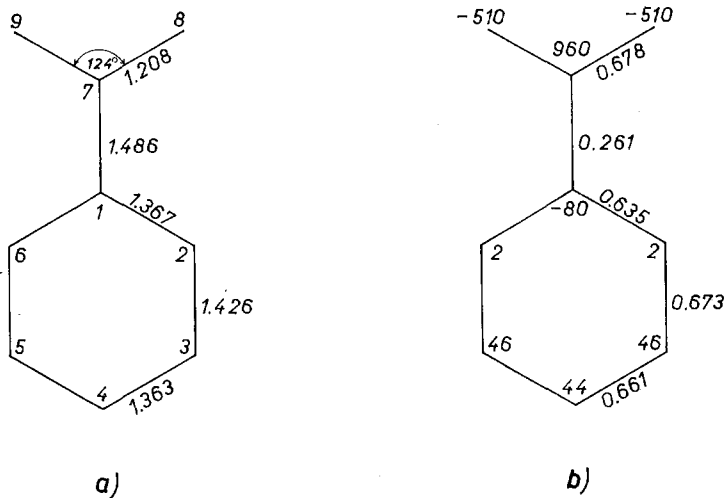


FIGURE 12(a). Adopted numbering of atoms and measured bond lengths<sup>128</sup> of nitrobenzene.

(b).  $\pi$  electron distribution (in units of 1/1000 |e|) and bond orders in the ground state<sup>129,130</sup>. Negative numbers for the charges correspond to an excess of negative charge.

bond is the longest bond in the benzene ring. Similar discrepancies are found by comparing these bond lengths with the bond orders obtained from semiempirical-SCF molecular orbital calculations of the Pariser-Parr-Pople type (type *b*; see section I.B.).

As a theoretical basis for our discussion we use calculations by Labhart and the author<sup>129</sup>. Table 13 shows the SCF molecular orbitals obtained by a set of semiempirical parameters given in Table 14. These parameters were calibrated by previous calculations on benzene and on the nitro group.

$I_p'$  stands for the effective (calibrated) ionization potential of atom  $p$ ,  $\beta_{pq}$  for the core resonance integral of the bond  $pq$ , and  $\gamma_{pq}$  for the electron repulsion integral  $\int p(1)p(1)(e^2/r_{12})q(2)q(2) d\tau$ .

TABLE 13. SCF  $\pi$  orbitals of nitrobenzene<sup>180</sup>

Symmetry	$\varepsilon_i$	$n_i$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	N	O	O'	Benzene $D_{6h}$	Nitro $C_{2v}$
9	4.09		0.382	-0.385	0.421	-0.427	0.421	-0.385	-0.122	0.052	0.052	$b_{2g}$	
8	1.29		-0.515	0.208	0.260	-0.494	0.260	0.208	0.399	-0.233	-0.233	$e_{2u}$	
7	0.82		0.000	0.477	-0.522	0.000	0.522	-0.477	0.000	0.003	-0.003	$e_{2u}$	
6	-1.02		-0.220	0.286	0.071	-0.308	0.071	0.286	-0.553	0.434	0.434	$b_1^*$	
5	-10.61	2	0.000	-0.522	-0.477	0.000	0.477	0.522	0.000	-0.023	0.023	$e_{1g}$	
4	-10.70	2	0.553	0.219	-0.326	-0.583	-0.326	0.219	0.011	-0.152	-0.152	$e_{1g}$	
3	-12.01	2	0.000	0.019	0.013	0.000	-0.013	-0.019	0.000	-0.707	0.707	$a_2$	
2	-13.86	2	0.431	0.415	0.378	0.372	0.378	0.415	-0.076	-0.143	-0.143	$a_{2u}$	
1	-18.08	2	0.220	0.080	0.027	0.012	0.027	0.080	0.717	0.460	0.460	$b_1$	
	$\sum_{i=1}^{n_i} c_i^2$		1.080	0.998	0.954	0.956	0.954	0.998	1.040	1.510	1.510		
	free charges $q_p$		-0.080	+0.002	+0.046	+0.044	+0.046	+0.002	+0.960	-0.510	-0.510		

In the two last columns at right it is indicated to which nitro group or pure benzene orbital a given nitrobenzene orbital is most closely related. Semiempirical parameters used for the calculation are given in Table 14. The coefficients are rounded to the third decimal.

TABLE 14. Pariser-Parr-Pople parameters<sup>129</sup> for nitrobenzene and nitrosobenzene in eV.

$I_{N'}$ (nitro) = 24.80	$\gamma_{NN} = 12.27$	$\beta_{NO} = -3.05$	$\gamma_{NO} = 8.70$
$I_{N'}$ (nitroso) = 13.40		$\beta_{CN} = -2.00$	$\gamma_{CN} = 7.96$
$I_{O'}$ = 16.30	$\gamma_{OO} = 14.50$		$\gamma_{OO'} \text{ (nitro)} = 6.28$
$I_{C'}$ = 9.00	$\gamma_{CC} = 10.53$	$\beta_{CC} = -2.46$	$\gamma_{CC'} = 7.27$

Electron repulsion integrals beyond nearest neighbors are assessed from electrostatic models<sup>6\*</sup>.

The dipole moment of nitrobenzene is larger than that of nitromethane, in agreement with simple resonance pictures, namely in the gas phase 4.21 D<sup>131</sup>.

One may calculate the contribution of the  $\pi$ -electrons to the dipole moment from the charge distribution given in Table 13, according to the simple formula

$$\vec{\mu}_e = e \sum_p q_p \cdot \vec{r}_p \quad (7)$$

where  $\vec{r}_p$  is the position vector of atom  $p$ . One obtains the value of 4.74 D, which is somewhat too large, as the contribution of the  $\sigma$ -electrons, while very probably smaller, certainly is not in the opposite direction.

If we estimate the ionization potential of nitrobenzene from the eigenvalue of the highest filled molecular orbital, -10.61 eV, we find a difference of 0.45 eV with the experimental value of 10.15 eV<sup>132</sup>. It then appears that the electronegativity of the nitro group has been somewhat overemphasized. The electronic absorption spectrum of nitrobenzene has been measured down to 155 m $\mu$  in the gas phase by Nagakura and coworkers<sup>133</sup>, as shown in Figure 13. Labhart has experimentally determined the polarization of the transitions above 220 m $\mu$  by electrochromism<sup>134,135</sup> in  $n$ -hexane solution. This method may be applied to solute molecules with a dipole moment of at least 2 D. If a static electric field is applied to the solution the electric dipoles of the solute molecules will tend to orient themselves parallel to the field lines. The average orientation of these molecules with respect to the external field will thus be

\* The calculated charge distribution and dipole moment for nitrobenzene given in reference 129 corresponds to an effective ionization potential for oxygen of 16.70 eV and not, as erroneously indicated, 16.30 eV. Upon reexamination of some of the calculations of reference 129 an error was furthermore found in the computation of the charge distributions of excited states. An Erratum has been published in *Helv. chim. Acta*, **51**, 204 (1968). All values given in this text are corrected values.



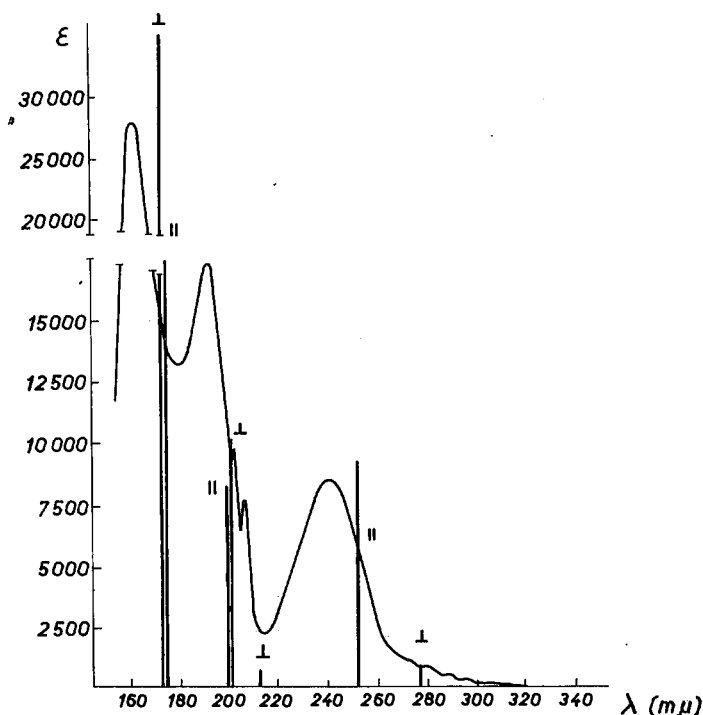


FIGURE 13. Gas-phase UV spectrum of nitrobenzene<sup>133</sup>, and calculated transitions<sup>130</sup>.

known. Now plane-polarized light is shone through the solution. The angle of the plane of polarization with respect to the direction of the electric field is changed by the observer, until the maximum of the absorption occurs. This gives us the polarization of that particular transition with respect to the dipole moment of the molecule. Figure 14 shows how the spectrum of nitrobenzene may be separated into components parallel and components perpendicular to the dipole moment. The weak transition at longest wavelength, which is polarized parallel to the dipole moment, has very probably  $n-\pi^*$  character. Its intensity may be due to vibronic interaction, leading to borrowing from  $\pi-\pi^*$  transitions. That is, if the NO<sub>2</sub> group gets twisted out of the plane of the molecule, the nonbonding orbital  $\sigma a_1$  mixes with  $\pi$  orbitals of symmetry  $a_2$  (see Tables 10 and 13).

A calculation based on the orbitals of Table 13 and taking into account the interaction between the 16 lowest singly excited configurations enables one to predict the  $\pi-\pi^*$  transitions as shown in

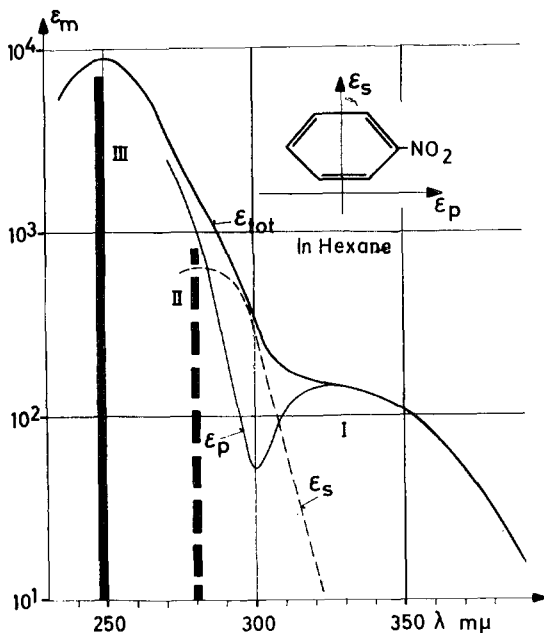


FIGURE 14. Near-UV spectrum of nitrobenzene in hexane. Resolution of the spectrum into bands polarized perpendicularly and parallel to the molecular dipole moment<sup>129,134</sup>.

Figure 13. The predicted transition at 277  $m\mu$  is polarized perpendicular to the molecular axis, while the transition at 252  $m\mu$  is polarized parallel. Both transitions have a dominant charge transfer character. The predicted absorption near 280  $m\mu$  also shows an appreciable component of the original benzene  ${}^1A_{1g} - {}^1B_{2u}({}^1L_b)$  transition (Explanatory details on the benzene transitions are contained in section III.A.2).

The calculated weak transition at 214  $m\mu$  is strongly related to the local  $a_2-b_1^*$  transition in the unconjugated nitro group (as for instance in nitromethane). Of the two predicted absorptions at 201 and 200  $m\mu$  respectively, the perpendicular one is strongly mixed, but nevertheless seems to contain an appreciable component of the benzene  ${}^1A_{1g} - {}^1B_{2u}$  transition; the parallel one is related to the benzene  ${}^1A_{1g} - {}^1B_{1u}$  transition. Finally, the predicted absorptions near 170  $m\mu$  appear to derive mainly from the  ${}^1A_{1g} - {}^1E_{1u}({}^1B_{a,b})$  transitions in benzene. The relative length of the lines in Figures 13 and 14 for each transition  $i-j$  are drawn proportional to the calculated

oscillator strengths  $f_{ij}$  (see footnote\*). However, the 277 m $\mu$  transition is adjusted to correspond to an  $\epsilon_{\max}$  value of 640. Upon comparison with the observed spectrum one notices that the predicted 250 m $\mu$  transition actually appears at 240 m $\mu$  in the gas phase, and the predicted transitions near 200 m $\mu$  probably correspond to the main part of the observed 190 m $\mu$  band. In general, there seems nevertheless to be qualitative agreement both with experiment and also with the theoretical predictions by Nagakura and coworkers<sup>133</sup>, which are based on a rather different quantum mechanical model of coupled molecular fragments. See also the theoretical treatment by Matsuoka and I'Haya<sup>136</sup>.

It has generally proven difficult to carry out our calculations on  $n-\pi^*$  transitions in larger molecules, nitrobenzene being no exception<sup>137</sup>. This is due to the fact that the nonbonding orbitals have  $\sigma$  symmetry. Strictly speaking, all  $\sigma$  valence electrons should be included in the calculation, thereby greatly increasing the computational labor.

The  $n-\pi^*$  transition in nitrobenzene shows a marked insensitivity to the polarity of solvents. Probably the actual displacement of charges in that transition is small. In contrast to the  $n-\pi^*$  transition, the 240 m $\mu$  band shows a very strong solvent dependence, appears at 250 m $\mu$  in hexane and gets further shifted to the red in polar solvents. Bayliss and McRae<sup>138</sup>, having also already interpreted this absorption as an intramolecular charge transfer band, predicted that the dipole moment of the corresponding excited state should be greater than in the ground state. In general, if the dipole moment decreases or changes sign in the excited state, there is a blue shift, if it increases, a red shift is encountered. Abe<sup>139</sup> has sought a direct quantitative relation between solvent shift and dipole moment in the excited state. He considers a system of  $N$  identical solvent molecules and one solute molecule and estimates the Van der Waals energy of the system when the solute molecule is in its ground state, and when the solute molecule is in its excited state. This difference in

\* Experimentally the oscillator strength of a band is given as  $f = 4.319 \times 10^{-19} \int \epsilon dv$  and is roughly proportional to  $\epsilon_{\max}$ ; the contribution of a transition  $i-j$  to  $f$  may be calculated as

$$f_{ij} = 4.703 \times 10^{29} \nu_{ij} |M_{ij}|^2; \quad \vec{M}_{ij} = e \sum_k \int \Psi_i^* Z_k \vec{r}_k \Psi_j d\tau.$$

$\nu_{ij}$  represents the transition frequency in cm<sup>-1</sup>,  $\Psi_i$  and  $\Psi_j$  the wavefunctions for ground and excited state,  $\vec{r}_k$  the position vector in cm and  $Z_k e$  the charge of the  $k$ th particle in the molecule in electrostatic units. See also reference 26, pp. 7-9.

Van der Waals energy is, on one hand, related to the polarity of the solvent molecules and to the dipole moment of the solute molecule in ground and excited state, on the other hand, to the energy of transition. From measured spectral shifts of the  $240\text{ m}\mu$  transition in nitrobenzene the dipole moment of the excited state is estimated to be  $8.18\text{ D}^{129}$ .

The determination of dipole moments in excited states may be of direct chemical interest. There seems to exist a correlation between

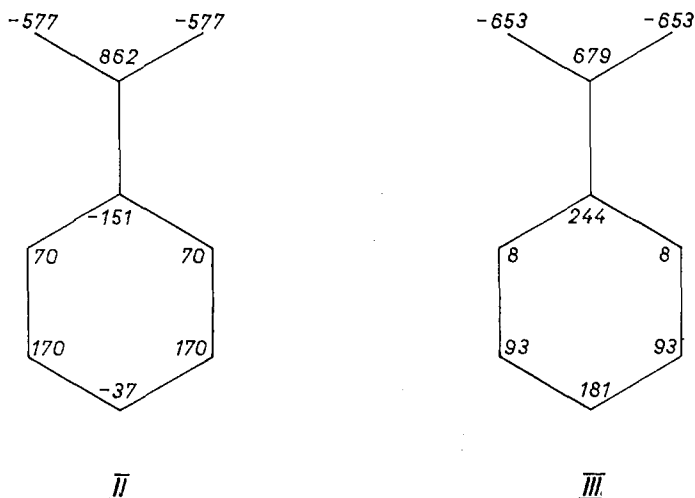


FIGURE 15. Distribution of  $\pi$  electron density (in units of  $1/1000 |e|$ ) in the first two excited  $\pi\text{-}\pi^*$  states of nitrobenzene<sup>129,130</sup>.

the  $\pi$  electron charge distribution in unsaturated systems and their proneness to electrophilic or nucleophilic addition or substitution at the individual atomic sites. In the electronically excited states the charge distribution is of course different from that of the ground state, and one may also assume the molecule to react differently chemically. In the same way as for the ground state, comparisons between the experimentally deduced dipole moment and the calculated one makes it possible to draw some conclusions on the charge distribution. However, the molecule must remain sufficiently long in the excited state to be able to undergo reaction. That is, the lifetime of the excited state must be at least of the order of the periods of vibration of the nuclei. In sufficiently dilute solution this condition is generally fulfilled for the lowest electronically excited

state. Lippert<sup>140</sup> has related the difference between the dipole moment of the ground and lowest excited singlet state to the shift of the absorption and fluorescence maxima in various solvents. As nitrobenzene does not fluoresce, Lippert's method can not be applied to this molecule. It is however applicable to some substituted nitrobenzenes.

Labhart<sup>134, 141, 142</sup> and Czekalla, Liptay and Wick<sup>143, 144</sup> have determined dipole moments of excited states from band shifts in an applied electric field. How such a band shift is caused may be visualized in Figure 16 for a simple case like nitrobenzene when the

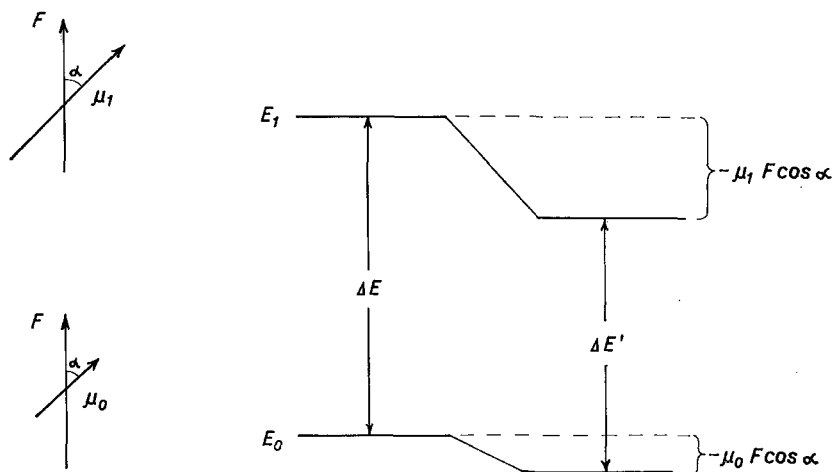


FIGURE 16. Line shifts in an electric field caused by changes of the dipole moment upon optical excitation<sup>141</sup>. In the case shown, ground and excited state dipole moments are assumed to be parallel to each other.

dipole moments in the ground and excited states are parallel. The energy of transition in the absence of the field is  $\Delta E = E_1 - E_0$ ; in the presence of the field

$$\begin{aligned} \Delta E' &= (E_1 - \mu_1 F \cos \alpha) - (E_0 - \mu_0 F \cos \alpha) \\ &= \Delta E - F(\mu_1 - \mu_0) \cos \alpha, \quad (8) \end{aligned}$$

where  $F$  designates the applied field strength,  $\mu_0$  and  $\mu_1$  symbolize the dipole moments in the ground and excited states and  $\alpha$  the angle between dipole moment and the direction of the applied field. Results of these measurements and of molecular orbital calculations for nitrobenzene are shown in Table 15. The calculated dipole moment for III seems to be too large, but the general trend is

TABLE 15. Dipole moment of nitrobenzene in ground and in excited states

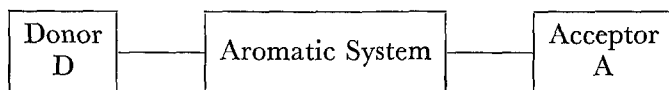
State	$\lambda(\text{m}\mu)$ hexane	$\vec{\mu}_{\text{exp}}(\text{D})$	$\vec{\mu}_{\text{calc.}}(\text{D})$
G		4.21 <sup>a</sup>	4.8
II	280	$9.0 \pm 2.0^b$	8.7
III	250	8.18 <sup>c</sup>	12.4

<sup>a</sup> Reference 131, <sup>b</sup> reference 129, <sup>c</sup>reference 139.

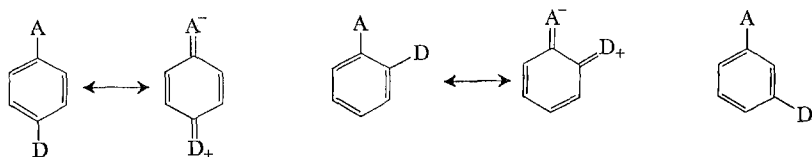
correctly predicted. One must, however, remember that in nitrobenzene the lowest singlet excited state (I), which is of interest photochemically, is the  $n-\pi^*$  state<sup>145</sup>, the dipole moment of which is not easily accessible either to experimental or to theoretical determinations.

## 2. The electronic properties of substituted nitrobenzenes

As is well known, substituents of aromatic systems are generally classified as electron donating, D, or as electron attracting, A. The electron donating property increases with decreasing ionization potential of the substituent. The electron accepting property is characterized by the electron affinity of the substituent. The nitro group is typically electron attracting, as is correctly reflected in Figure 12. According to this calculation, the substituent has withdrawn 0.06 electrons from the benzene ring in the electronic ground state. If we consider nitrobenzene which has been further substituted by a typical electron donor, such as dimethylamino, the molecule may then be represented by the scheme:



From the point of view of resonance theory one expects ionic structures to contribute significantly to the basic Kekulé structures in the case of ortho- and para-substituted nitrobenzene. On the other hand, no equivalent ionic structure may be written in the meta-substituted case:



One thus might conclude that the electronic properties of the *m*-substituted molecule are quite different from those of the *p*- and *o*-substituted ones. As has been pointed out by Grinter and Heilbrönnner<sup>146</sup>, this conclusion is wrong. The spectra in the visible and near UV of *o*- and *m*-*N*-dimethylnitroaniline resemble each other quite strongly, while that of the *p*-compound exhibits rather different features. As the above-mentioned authors have shown, these aspects of the electronic structure may be satisfactorily interpreted by a simple molecular orbital picture in which the interaction between the benzene ring, the electron donor and the electron acceptor is assessed. The donor is characterized by a doubly filled, bonding  $\pi$  orbital D, the acceptor by an antibonding, empty  $\pi$  orbital A, the benzene ring by the six orbitals  $a_{2u}$ ,  $e_{1g}^{\pm}$ ,  $e_{2u}^{\pm}$ ,  $b_{2g}$ , as shown in Figure 17. The orbital D corresponds to the  $2p_z$  function of the nitrogen atom in the amino group, the orbital A to the  $b_1^*$  orbital of the nitro group (the electrons in the lower  $\pi$  orbitals  $b_1$  and  $a_2$  of the nitro group are here ignored). The electron distribution shown in Figure 17 corresponds to the ground configuration  $\Gamma$ .

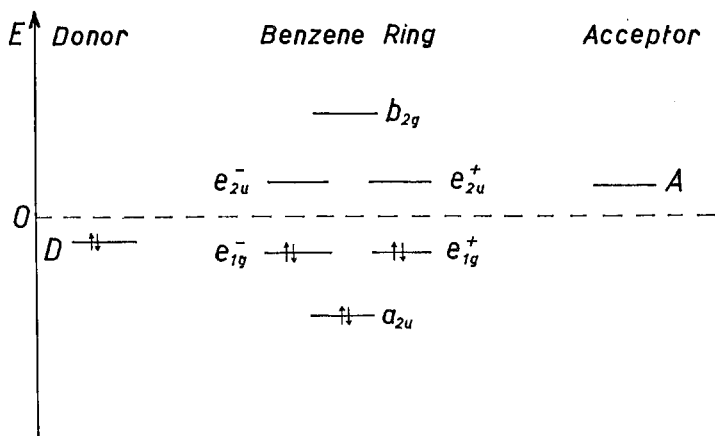


FIGURE 17. Orbital scheme for a benzene ring interacting with an electron donor (D) and an electron acceptor (A). In the ground configuration the orbitals are occupied as here shown.

The following singly excited configurations are now taken into account (1): four singly excited configurations within the benzene ring, namely from  $e_{1g}^-$  to  $e_{2u}^-$  or  $e_{2u}^+$ , from  $e_{1g}^+$  to  $e_{2u}^-$  or  $e_{2u}^+$ . These configurations describe the first excited states of benzene

(the singlet states are in Platt's notation  $^1L_a$ ,  $^1L_b$ ,  $^1B_a$ ,  $^1B_b$ , in group theoretical notation  $^1B_{1u}$ ,  $^1B_{2u}$ ,  $^1E_{1u}$ ) and will be designated collectively by  $\Lambda$ . (2): two charge transfer excitations from the donor  $D$  to the ring, namely to  $e_{2u}^-$  or  $e_{2u}^+$ , collectively designated by  $T_D$ . (3): two charge transfer excitations from the ring to the acceptor, namely from  $e_{1g}^-$  or  $e_{1g}^+$  to  $A$ , designated by  $T^A$ . (4): finally, a configuration is considered in which an electron has been transferred from  $D$  to  $A$ ,  $T_D^A$ .

Assuming an ionization potential of the donor of +10 eV, an electron affinity of the acceptor of -1 eV, and a coupling parameter  $\beta$  between the fragments of -2.5 eV, Grinter and Heilbronner obtain the results shown in Table 16. The ionization potential and electron affinity of benzene are taken from experiment, as well as the energies of the local benzene excitations.

TABLE 16. The contribution in percent of the various configurations described in the text to the ground and first excited states of benzene substituted by a strong electron donor and a strong electron acceptor, as calculated by Grinter and Heilbronner<sup>146</sup>.

State	$\Gamma$	$\Lambda$	$T_D$	$T^A$	$T_D^A$	$\lambda_{\max}(m\mu)$ calc.
$G(A_{1g})_o$	78	1	8	12	—	
$G(A_{1g})_m$	80	—	8	12	—	
$G(A_{1g})_p$	76	2	9	13	1	
$I_o$	3	31	13	32	21	410
$I_m$	—	32	19	39	9	400
$I_p$	—	62	6	32	—	320

These results exhibit clearly the resemblance between the electronic structures of the *o*- and *m*-compounds. In the first excited state the *p*-compound shows a stronger contribution of locally excited benzene configurations. However, the absolute values of the numbers obtained are very strongly dependent on the choice of parameters.

Doub and Vandenberg<sup>147-149</sup> have measured the near-UV spectra of mono-, di- and tri-substituted benzene derivatives systematically by going from weak to strong substituents. Stevenson<sup>150</sup> has discussed these results theoretically, based mainly on previous work of Förster<sup>151</sup> and Petruska<sup>152</sup>. It seems that the absorption appearing at longest wavelength in the *p*-disubstituted donor-acceptor-compound 'grows out' of the  $^1A_{1g}$ - $^1L_a$  transition of benzene (204  $m\mu$ ,  $\epsilon = 7400$ ). Stevenson assumes the  $^1L_a$  state to mix

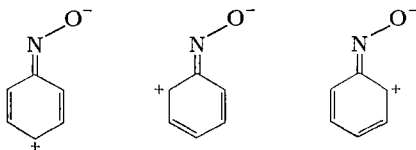


mainly with a quinoid substituent-to-substituent charge transfer state and thereby to be drastically shifted to the red. This point is not borne out by the results of Grinter and Heilbronner, according to which the  $T_D^A$  configuration does not appear to play an important role in the first excited state of the *p*-compound. In both the *o*- and *m*-disubstituted molecules the first absorption is considered by Stevenson to be mainly related to the  $^1A_{1g}-^1L_b$  transition of unsubstituted benzene (250 m $\mu$ ,  $\epsilon = 200$ ).

Measurements of the polarizations of transitions reveal the 380 m $\mu$  band in *p*-nitroaniline to be in fact the superposition of two absorptions: a stronger one parallel to the symmetry axis and a weaker one perpendicular<sup>129</sup>. The stronger absorption is related by symmetry to the  $^1A_{1g}-^1L_a$  transition in benzene and contains an appreciable  $T_D^A$ -contribution. The qualitative sequence of transitions seems to be correctly predicted by the calculation as well as the relative magnitude of dipole moments. The absolute values show, as in the case of nitrobenzene itself, that the effect of the substituents has been somewhat overrated. Unfortunately, no investigations of this kind have been carried out for *o*- and *m*-nitroaniline.

### 3. The electronic structure of nitrosobenzene and substituted nitrosobenzene

In analogy to the nitro group the nitroso substituent also acts as a strong electron acceptor. This is again well reflected by simple resonance pictures.



Observed and calculated data are shown in Figure 19. The calculated  $\pi$  dipole moment is, interestingly, predicted to be smaller than the observed total one. It nonetheless appears that the nitroso group has withdrawn 0.10 electrons from the benzene ring. The directions of polarization of the absorption bands are measured with respect to the dipole moment. However, because of the low symmetry of the molecule, the direction of the dipole moment with respect to the molecular frame is not known and must be calculated. With regard to their polarizations and relative strengths the transitions are

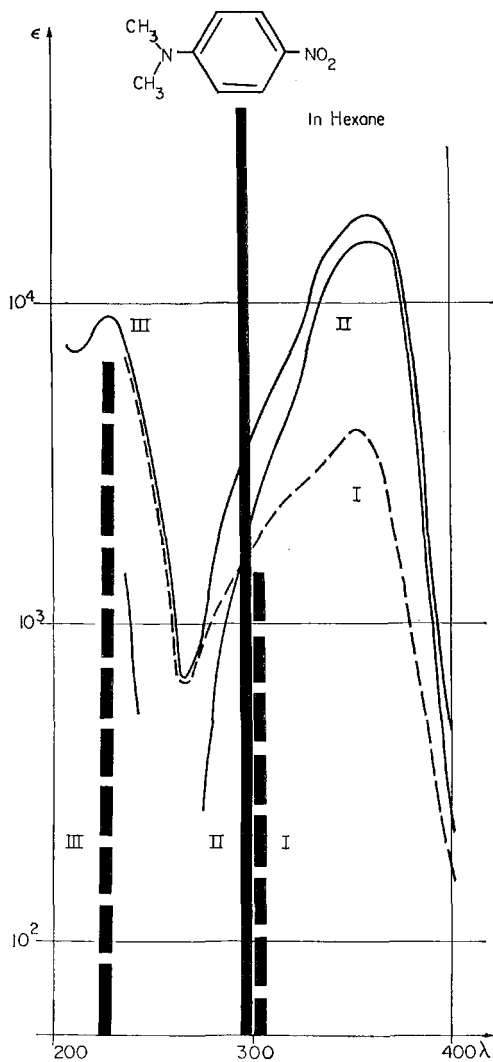


FIGURE 18. Measured and calculated<sup>129</sup> polarizations of the longest-wavelength transitions I, II, III of *p*-*N,N*-dimethylnitroaniline. The transitions I and III are polarized perpendicularly to the molecular axis. The calculated sequence of transitions agrees qualitatively with the observed one.

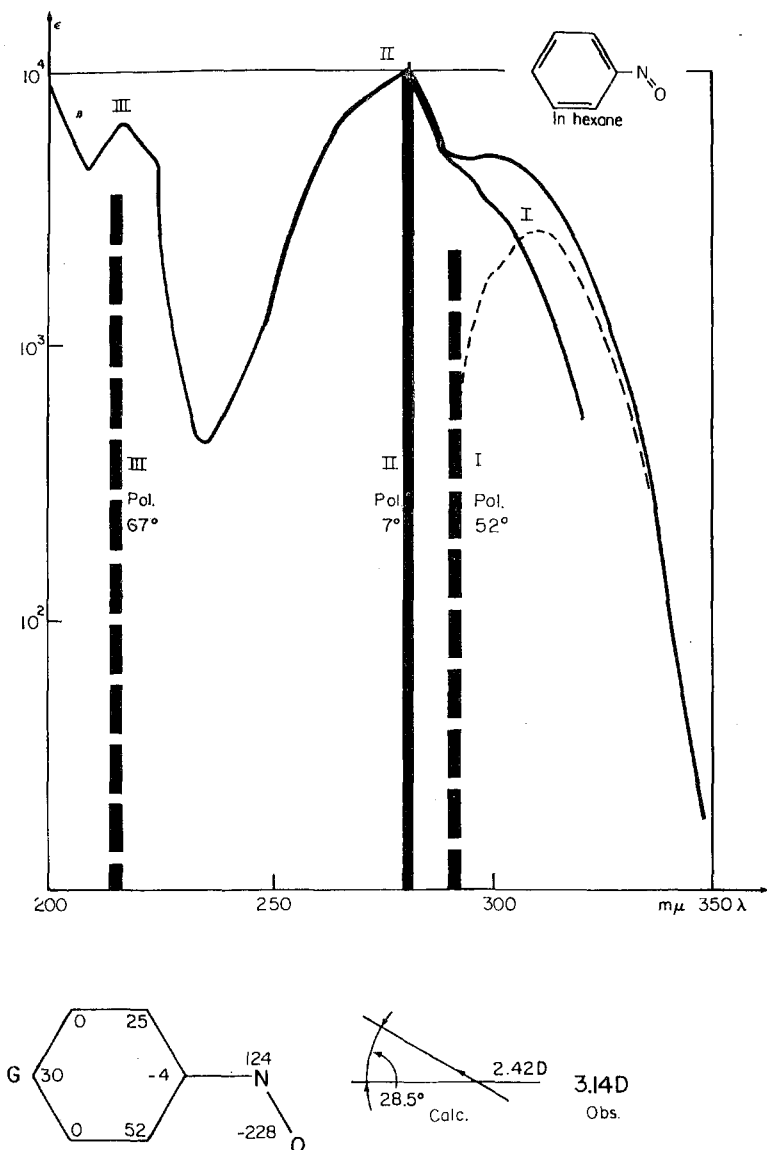


FIGURE 19. Measured and calculated<sup>129</sup> polarizations of the longest-wavelength transitions of nitrosobenzene. The dipole moment is of course no longer parallel to the C—N axis. The measured and calculated polarizations of the transitions are indicated with respect to the dipole moment. Below, the calculated ground state  $\pi$  electron distribution is given (in units of  $1/1000 |\epsilon|$ ), as well as the calculated  $\pi$  dipole moment and observed total dipole moment.

correctly predicted. However, the calculated energy of the transition G-I is too high. The  $n-\pi^*$  transition, appearing at  $755\text{ m}\mu$  is not shown in Figure 19.

The general discussion of the previous section is also valid for *p*-nitrosoaniline. The first transition is definitely polarized along the molecular axis and contains a particularly strong substituent-to-substituent charge-transfer ( $T_D^A$ ) component.

## **B. Magnetic Properties of Nitro and Nitroso Aromatic Compounds**

### **I. Pi-electron density and NMR chemical shifts**

Nuclear magnetic resonance spectroscopy is a method of great interest and of great promise to gain further insight into the distribution of electron densities in molecules. In section II.C.2 we have briefly discussed the inductive effect of the nitro group in an alkane chain and the anisotropy of the diamagnetic shielding as assessed from proton resonance measurements. In this section we will give an outline of the relationship between  $\pi$  electronic structure and chemical shifts of proton,  $C^{13}$ ,  $N^{15}$  and  $N^{14}$  resonances in nitro and nitroso aromatic compounds.

As is well known, the nuclear magnetic resonance frequency  $\nu$  is related to the spin magnetic moment of a nucleus  $\mu$ , the value of the nuclear spin  $I$  and the effective magnetic field at the nucleus  $H$  by the formula

$$\nu = \mu H / h \quad (9)$$

where  $h$  is Planck's constant. The effective magnetic field may be written

$$H = H_0(1 - \sigma) \quad (10)$$

where  $\sigma$  is the shielding constant,  $H_0$  the applied external field and  $H_0 \cdot \sigma$  the chemical shift with reference to the free nucleus<sup>153,154</sup>. The shielding constant for a particular nucleus  $\sigma_i$  in a molecule may conveniently be split up into several parts<sup>155</sup>:

$$\sigma_i = \sigma_i^D + \sigma_i^P + \sigma_i^A \quad (11)$$

$\sigma_i^D$  represents the diamagnetic contribution from the electron density on the  $i$ th atom,  $\sigma_i^P$  is the local paramagnetic correction due to the immediate environment, and  $\sigma_i^A$  stands for the contributions from the electron density on other atoms in the molecule.  $\sigma_i^A$  is here assumed also to include anisotropic effects arising from the collective interaction of all electrons in the molecule, such as 'ring current'

effects. In addition, the influence of the medium surrounding the molecule must also be taken into account.

Diehl<sup>156</sup> has studied the proton magnetic resonance spectra of substituted benzenes, finding an additivity rule for the influence of the substituents and correlating his results with Hammett-parameters<sup>157</sup>. Wu and Dailey<sup>155</sup> have related experimental proton, C<sup>13</sup> and fluorine chemical shifts to  $\pi$  electron densities in substituted benzenes. We will base our discussion mainly on the work of these latter authors, focusing our attention on proton and C<sup>13</sup> chemical shifts in nitro compounds.

In the case of proton chemical shifts the paramagnetic term  $\sigma_i^P$  is small, low lying excited states being absent in most bonds involving protons. In an aromatic molecule the proton chemical shift with benzene as reference standard,  $\Delta\sigma_i^H$ , due to the polarization of the C—H bond, is related to the  $\pi$  electron density  $\rho_i$  on the carbon atom. As has been shown theoretically<sup>158,159</sup> this may be written

$$\Delta\sigma_i^H = K(\rho_i - 1) \quad (12)$$

$K$  is then taken as a constant and has been calibrated on cyclopentadienyl anion, benzene, tropylium cation and cyclooctatetraene dianion. After correction for ring current effects in these systems, as well as for influence of the solvent,  $K$  is found to be 8.08 ppm/electron<sup>155</sup>. If the above equation is fulfilled, it then implies that "ring-current" effects are constant within the series under investigation and that local diamagnetic effects are dominant in a relative sense.

For C<sup>13</sup> chemical shifts a similar relationship has been worked out by Karplus and Pople<sup>160</sup>. Namely, in ppm-units:

$$\Delta\sigma_i^C \approx (86.7 + 46.0\lambda_H)(\rho_i - 1) + 46.0(F_i - 0.399) \quad (13)$$

where  $\lambda_H$  is a polarity parameter for the C—H bond and may be assumed to be small, and  $F_i$  is the free valence\* of the shielded

Pi-electron densities and free valences may be calculated from Hückel (type *d*) calculations, using the set of parameters for the carbon *i*.

\* The free valence on an atom *i* is defined as

$$F_i = N_{\max} - N_i$$

where  $N_i$  is the sum of the orders of all bonds joining atom *i* and  $N_{\max}$  is the maximum value possible, taken as  $\sqrt{3}$  <sup>9</sup>.

heteroatoms given by Streitwieser<sup>9</sup> (see Table 17). Calculated chemical shifts are then obtained using formulae (12) and (13). Experimental data in Table 18 show the influence of strongly electron donating and strongly electron attracting substituents. Wu and Dailey have standardized experimental  $\Delta\sigma^H$ -values to conform to the shielding scale of Martin and Dailey<sup>163</sup>. To a large

TABLE 17. Hückel parameters according to Streitwieser. The coulomb integral for a heteroatom X is given as  $\alpha_X = \alpha + h_X\beta$ , the resonance integral for a bond X—Y as  $\beta_{X-Y} = k_{X-Y}\beta$ . The parameters  $\alpha$  and  $\beta$  for benzene are taken as standard values. If the atom X contributes one  $\pi$  electron, it is designated by  $\dot{X}$ , if it contributes two  $\pi$  electrons,  $\ddot{X}$ .

Coulomb integral $\alpha_X$	Resonance integral $\beta_{X-Y}$
$h_{\dot{N}} = 0.5$	$k_{C-N} = 0.8$
$h_{\ddot{N}} = 1.5$	$k_{C=N} = 1.0$
$h_{\dot{O}} = 1.0$	$k_{N-O} = 0.7$
$h_{\ddot{O}} = 2.0$	$k_{C-O} = 0.8$
	$k_{C=O} = 1.0$

extent this takes into account solvent effects. Such standardized values are compared to the theoretical ones in Table 19. Wu and Dailey conclude that in the para-position of the monosubstituted benzene the qualitative trend both for proton and  $C^{13}$  resonance is correctly reproduced by the calculated values, showing that variations in the  $\pi$  electron density are probably mainly responsible for variations in the chemical shift. In the ortho-position, the observed larger upfield shift for the carbon resonance in Ph-NO<sub>2</sub> is to be noted. In the meta-positions, the chemical shifts are in general small

TABLE 18. Experimental proton chemical shifts in p.p.m. for mono-substituted benzene (with benzene as standard), measured in cyclohexane. Note the difference between the influence of electron acceptors NO<sub>2</sub> and NO, and the donor substituent NH<sub>2</sub>.

Substituent	Para	Meta	Ortho	Ref.
NH <sub>2</sub>	+0.62	+0.20	+0.75	161
NO <sub>2</sub>	-0.33	-0.21	-0.95	161
NO	-0.31	-0.26	-0.56	162

TABLE 19. Proton and C<sup>13</sup> resonance data on nitrobenzene, aniline, *p*-dinitrobenzene, and *p*-diaminobenzene.

Substituent	Position	$\rho_i$	$F_i$	$\Delta\sigma_{\text{calc.}}^{\text{H}}$	$\Delta\sigma_{\text{obs.}}^{\text{H}}$	$\Delta\sigma_{\text{calc.}}^{\text{C}}$	$\Delta\sigma_{\text{obs.}}^{\text{C}}$
NO <sub>2</sub>	<i>p</i>	0.92860	0.44654	-0.577	-0.290	-4.00	-6.00
	<i>m</i>	0.99499	0.39773	-0.040	-0.155	-0.49	-0.80
	<i>o</i>	0.95045	0.45698	-0.400	-0.955	-1.63	5.30
H <sub>2</sub> N	<i>p</i>	1.03667	0.40655	0.296	0.760	3.53	9.5
	<i>m</i>	0.99773	0.39661	-0.018	0.271	-0.31	-1.3
	<i>o</i>	1.04843	0.42211	0.391	0.768	5.26	12.4
<i>p</i> -dinitro	<i>o</i>	0.95315	0.45011	-0.379	-1.147		
<i>p</i> -diamino	<i>o</i>	1.04536	0.42080	0.366	0.950 <sup>a</sup>		

<sup>a</sup> Calculated from additivity relationship of reference 163.

and correlations between the different types of chemical shifts are more difficult to establish.

Further discussions on C<sup>13</sup> chemical shifts in substituted benzenes have been given by Maciel and Natterstad<sup>164</sup>. Lauterbur<sup>165</sup> has studied the steric inhibition of conjugation in methylnitrobenzenes. In particular, he has found that in the orthomethyl compounds there is a marked increase in para-carbon shieldings, due to the reduced  $\pi$  electron-withdrawing effect of the nitro group.

Lambert and Roberts<sup>166</sup> have studied N<sup>15</sup> chemical shifts in oxygen-nitrogen compounds. In contrast to the proton and carbon resonances, it appears that in nitrogen resonance the paramagnetic term  $\sigma_{\text{N}}^{\text{P}}$  may become predominant. This paramagnetism can be attributed to the existence of low-lying magnetic dipole allowed transitions involving orbitals on the nitrogen atom, such as  $n-\pi^*$  transitions<sup>167,168</sup>. Under the influence of the magnetic field such excited states mix with the ground state and give rise to a paramagnetic contribution to the susceptibility. The lower the  $n-\pi^*$  transition and the greater the contributions of nitrogen atomic functions to the  $n$  and  $\pi^*$  orbitals, the stronger should be the paramagnetic shift in the nitrogen resonance. Theoretical estimates show that the influence of the molecular environment on the diamagnetic contribution  $\sigma_{\text{N}}^{\text{D}}$  is probably much smaller than the actually observed variations in chemical shifts. On the other hand, these experimental chemical shifts correlate quite well with data on the  $n-\pi^*$  transitions. Experimental results for nitrobenzene and nitrosobenzene, as given by Lambert and Roberts, are reproduced in Table 20.

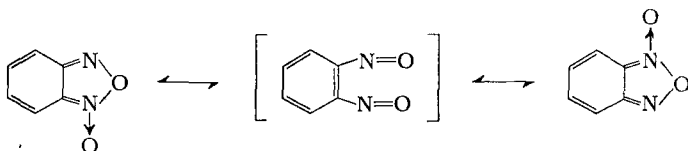
TABLE 20. The chemical shifts are taken from reference 166. They are downfield from external anhydrous ammonia.

	$\lambda_{n-\pi^*}(\text{m}\mu)$	$\text{N}^{15}$ shift (p.p.m.)
Nitrobenzene	330	-372
Nitrosobenzene	755	-913

$\text{N}^{15}$  chemical shifts may apparently be of help in the assignment of weak UV transitions, and the observation of  $n-\pi^*$  transitions may in turn facilitate the interpretation of nitrogen resonance data.

In the isotope  $\text{N}^{14}$ , nuclear quadrupole coupling broadens the resonance lines. In general, observed chemical shifts<sup>169,170</sup> correlate well with those for  $\text{N}^{15}$ , except in cases which have in common intramolecular barriers to rotation<sup>171</sup>. Incomplete spherical averaging of electrical field gradients lead to anomalously large chemical shifts for  $\text{N}^{14}$  in these latter cases.

An interesting application of  $\text{O}^{17}$  resonance has been made by Diehl and coworkers<sup>172</sup>, who have studied the tautomerism:



At room temperature ( $28^\circ$ ) two separate lines occur, confirming the nonequivalence of the O nuclei. At  $78^\circ$  only one line is observed showing rapid exchange. This exchange process probably goes over the dinitroso structure. From this temperature dependence the activation energy of the reaction is estimated to be  $17.2 \pm 1.5$  kcal/mole.

## 2. The radical anions of nitroaromatic compounds

The negative ions of nitroaromatic compounds, in particular of nitrobenzene and of substituted nitrobenzenes, have been investigated quite extensively<sup>173-183</sup>. The hyperfine splittings of the ESR lines due to the different nuclear spins in the molecule may be related to the  $\pi$  electronic structure (see also section II.B.1). Geske and Maki<sup>179</sup> have shown that there is some degree of correlation between the polarographic halfwave potentials of *m*- and *p*-substituted nitrobenzene and the nitrogen hyperfine splittings in its anion



radical, as well as with  $\sigma_0$  values of Taft and Lewis<sup>184</sup> and  $\sigma^n$  values of van Bekkum, Verkade, and Wepster<sup>185</sup>. Schug, Brown, and Karplus<sup>186</sup> have developed a simple model, based on valence bond theory, which permits the approximate superposition of the ESR results for mono-substituted benzenes to estimate the hyperfine constants of poly-substituted species. Rieger and Fraenkel<sup>187</sup> have carried out a study of nitrosubstituted benzene anions based on molecular orbital theory, which we will mention in somewhat more detail.

The starting point is, as mentioned previously, McConnell's relation<sup>47</sup>. In the case of protons we write

$$a_q^{\text{H}} = Q_{\text{CH}}^{\text{H}} \cdot \rho_q^{\pi} \quad (14)$$

where  $a_q^{\text{H}}$  is the hyperfine splitting (in Gauss) for the proton bonded to the  $q$ th carbon atom of the molecule,  $\rho_q^{\pi}$  is the  $\pi$  electron spin density on this carbon atom, and  $Q_{\text{CH}}^{\text{H}}$  is taken as a constant, with a value of  $-23.7$  G. In a first approximation the spin density on any carbon atom  $q$  is simply given by the square of the  $q$ th LCAO coefficient  $c_{uq}$  of the molecular orbital containing the unpaired electron, namely, of the lowest empty orbital of the neutral molecule:

$$\rho_q^{\pi} \approx c_{uq}^2$$

To this degree of approximation the spin density is considered to be equal to the Hückel charge density. However, this limited approach is totally unable to account for the spectra of certain radicals. For instance, in the pyrene anion the charge density of the unpaired electron vanishes at the two terminal carbon atoms lying on one of the vertical planes of symmetry, yet the protons attached to these carbon atoms contribute to the hyperfine structure<sup>45</sup>. This can only be explained by assuming negative spin densities at these sites. The occurrence of negative spin densities may be thought of as arising through the correlation of electrons of opposite spin, which is neglected in a simple Hückel calculation, or even in restricted SCF procedures. This correlation may be taken into account either by configuration interaction<sup>188</sup>, or by assuming different spatial orbitals for electrons of different spins. Thus, valence-bond theory<sup>189</sup> has had some success in interpreting ESR data, where simple MO-methods at first failed. McLachlan has developed a perturbation calculation which allows for the inclusion of limited configuration interaction within the framework of simple Hückel MO-theory<sup>190</sup>.

Rieger and Fraenkel adopt McLachlan's procedure and write<sup>191</sup>

$$\rho_a^\pi = c_{uq}^2 - \lambda \sum_s \pi_{qs} c_{us} \quad (15)$$

where  $\pi_{qs}$  is the atom-atom polarizability of Hückel-theory\*,  $\lambda$  is taken as an empirical constant and is given the value  $1.2\beta$ . Now there still remains the problem of finding suitable semi-empirical parameters for the Hückel calculations. Rieger and Fraenkel have calibrated their calculated spin densities, corrected by the McLachlan procedure, to the ones experimentally deduced from the proton splittings in nitrobenzene in *N,N*-dimethylformamide solution. Based on this, they adopt the parameters for the nitro group given in Table 21.

TABLE 21. Hückel parameters for nitro and amino, as adopted by Rieger and Fraenkel<sup>187</sup>. Values for nitro are calibrated on ESR data for nitrobenzene. Compare these values with the ones given in Table 17.

Coulomb integrals	Resonance integrals
$h_N^{\cdot}(\text{nitro}) = 2.2$	$k_{C-N}(\text{nitro}) = 1.2$
$h_N^{\cdot}(\text{amino}) = 1.7$	$k_{C-N}(\text{amino}) = 0.7$
$h_O(\text{nitro}) = 1.4$	$k_{N-O}(\text{nitro}) = 1.67$

ESR spectra of nitroaromatic compounds are very sensitive to solvent effects and to the method of generation of the radical ions (by electrolytic, or by chemical reduction). Data for different compounds within this group may only be compared and interpreted theoretically with the same set of semi-empirical parameters if it has been measured under the same experimental conditions. Taking these facts into account Rieger and Fraenkel succeed in correlating measured and calculated hyperfine splittings in a large class of substituted nitrobenzenes. A least-squares analysis of MO energies *versus* experimental polarographic half-wave potentials yields the

\* The atom-atom polarizability between atoms  $q$  and  $s$  is defined as

$$\pi_{qs} = -4 \sum_i \sum_j (c_{iq} c_{js} c_{is} c_{jq}) / (e_i - e_j)$$

where the index  $i$  runs over occupied molecular orbitals of the neutral molecule in the ground state, and the index  $j$  refers to vacant orbitals. The  $c_{iq}$ ,  $c_{js}$  are orbital coefficients and  $e_i$ ,  $e_j$  orbital energies in units of the carbon-carbon resonance integral  $\beta$ .

following results:

$$E_{\frac{1}{2}} = (0.24 \pm 0.17) - (2.28 \pm 0.50)x$$

where  $x$  is the energy of the lowest vacant orbital of the neutral molecule (see Table 22).

The hyperfine splitting arising from the nitrogen nucleus of the nitro group must be considered in a special way, as it appears to be not only dependent on the unpaired spin density at the nitrogen atom itself,  $\rho_N^\pi$ , but also at the adjacent carbon,  $\rho_C^\pi$ , and oxygen

TABLE 22. Energy of the lowest vacant orbital of the neutral molecule in units of  $\beta$ , and calculated polarographic half-wave potentials in volts, from reference 187. Experimental values are from the work by Maki and Geske<sup>179</sup>.

	$x$	$-E_{\frac{1}{2}}$ calc.	$-E_{\frac{1}{2}}$ exp.
Nitrobenzene	0.3787	1.10	1.15
1,4-Dinitrobenzene	0.1997	0.70	0.69
4-Nitroaniline	0.4066	1.17	1.36

atoms,  $\rho_O^\pi$ . Karplus and Fraenkel<sup>187,192</sup> have developed the following expression:

$$a^N(\text{nitro}) = (S^N + Q_{NC}^N + Q_{NO}^N)\rho_N^\pi + Q_{CN}^N\rho_C^\pi + 2Q_{ON}^N\rho_O^\pi \quad (16)$$

where  $S^N$  represents the contribution to the splitting from the nitrogen  $1s$  electrons and the  $Q$ 's account for the contribution of the  $2s$  electrons, due to indirect coupling effects. For instance,  $Q_{ON}^N$  is a constant which measures the indirect coupling of the  $\pi$  spin density on the oxygen atom with the nuclear spin of the nitrogen atom, *via* the electrons in the NO bond (see also section II.B.1). In the absence of theoretical values for these quantities,  $(S^N + Q_{NC}^N + 2Q_{NO}^N)$ ,  $Q_{CN}^N$  and  $Q_{ON}^N$  may be obtained by a least squares fit to experimental nitrogen splitting constants, assuming that the spin densities are given by the McLachlan procedure. The data obtained for a given set of molecules may then be used to predict the properties of other nitroaromatics (see Table 23). From 17 experimental values Rieger and Fraenkel find:

$$(S^N + Q_{NC}^N + 2Q_{NO}^N) = \pm(99.0 \pm 10.2)G \quad (17a)$$

$$Q_{ON}^N = \mp(35.8 \mp 5.9)G. \quad (17b)$$

It appears that  $Q_{ON}^N$  makes no statistically significant contribution,

TABLE 23. Spin densities and splitting constants  $a^N$  and  $a^H$  for nitrobenzene and for nitrobenzene substituted in the *p*-position by a strong electron acceptor, or a strong electron donor. All data are taken from reference 187. Calculated  $a^N$  values are deduced from formula (16),  $a^H$  values from formula (14). Measurements on 4-nitroaniline were carried out in acetonitrile, as given by Maki and Geske<sup>179</sup>. The other measurements were carried out in *N,N*-dimethylformamide. Notice the unusually low splitting constant for nitrogen in 1,4-dinitrobenzene.

	Position	Spin densities		Splitting constants	
		Hückel	McLachlan	calc.	exp.
Nitrobenzene	0	0.1947	0.1988		
	N	0.2257	0.2381	9.33	9.70
	1	0.0398	0.0071		
	2	0.1055	0.1414	3.35	3.36
	3	0.0049	-0.0480	1.14	1.07
1,4-Dinitrobenzene	4	0.1244	0.1704	4.04	4.03
	0	0.1104	0.1148		
	N	0.1041	0.1042	2.09	1.48
	1	0.0748	0.0796		
	2	0.0501	0.0434	1.03	1.12
4-Nitroaniline	0	0.1946	0.2004		
	N(nitro)	0.2405	0.2592	11.31	12.18
	4	0.0264	-0.0115		
	3	0.1071	0.1465	3.47	3.36
	2	0.0009	-0.0524	1.24	1.12
	1	0.1151	0.1534		
	N(amine)	0.0127	0.0098		1.12

and that the upper signs in (17*a*, *b*) must be taken. So finally one may write

$$a^N(\text{nitro}) = 99.0\rho_N^\pi - 71.6\rho_O^\pi \quad (18)$$

What happens when the nitro group gets twisted out of the plane of the benzene ring? Does the unpaired electron gradually drift onto the nitro group? Or does it stay in the benzene ring? Our knowledge about the electron attracting properties of the nitro group lets us suspect that the first alternative is the more probable one. This has indeed been confirmed experimentally by Geske and Ragle<sup>180</sup> in measurements on methyl-substituted nitrobenzenes, as shown in Table 24. The observed value of  $a^N$  for the highly hindered compounds approaches the one found in various nitroaliphatic anion radicals<sup>121</sup>, namely 24.2 to 25.7 gauss (see section II.C.2). Simultaneously the splitting constants for the ring protons gradually go to zero<sup>180,193</sup>. If we examine the lowest unfilled molecular orbital in

Table 13, we note that it is mainly related to the  $b_1^*$  orbital of the "free" nitro group. This is the orbital which contains the unpaired electron in the anion. Now, if by twisting the nitro group the conjugation is gradually interrupted, the molecular orbital will become more and more like the pure  $b_1^*$  orbital, thereby localizing the unpaired electron on the nitro group.

TABLE 24. Nitrogen splitting constant in methyl substituted nitrobenzenes<sup>180</sup>.  $a^N$  increases with growing steric hindrance. The solvent is acetonitrile. Notice the influence of the solvent by comparing the value of  $a^N$  for unsubstituted nitrobenzene indicated here with the one given in Table 23.

Methyl-position	$a^N$
—	10.32
4	10.79
3, 5	10.6
2	11.0
2, 3	11.7
2, 6	17.8
2, 3, 5, 6	20.4

The nitrogen splitting constant in 1,8-dinitronaphthalene<sup>184,195</sup> and in 1,4,5,8-tetranitronaphthalene<sup>194</sup> reflects the steric interaction between the nitro groups. In the latter compound Gerson and Adams found  $a^N$  to be temperature dependent.

ESR measurements are being increasingly applied to conformational problems. Thus in the anion radical of *p*-nitrobenzaldehyde the assignment of four instead of three proton splitting constants was interpreted as evidence that the carbonyl group is restricted to a configuration coplanar with the benzene ring<sup>179</sup>. Stone and Maki<sup>196</sup> concluded from ESR data that free rotation of the formyl group in *o*-nitrobenzaldehyde is unlikely. More recently, McKinney and Geske have interpreted the spectrum of the tetraisopropylnitrobenzene anion radical in terms of two discrete conformational isomers existing in thermodynamic equilibrium<sup>197</sup>. These authors have summarized the different types of ESR studies which have led to structural conclusions:

(a) conformational inferences of restricted intramolecular motion based on the magnitudes of splitting constants;

(b) conformational evidence for restricted intramolecular motion based on the number of splitting constants observed, arising from an asymmetry of the radical;

(c) conformational conclusions based on the observation of physically distinguishable conformers.

The ESR spectrum of nitrosobenzene anion has been measured in ammonia<sup>198</sup>. Due to the asymmetry of the molecule the spectrum shows two ortho and two meta proton coupling constants (see Table 25).

TABLE 25. Experimental splitting constants for nitrobenzene and nitrosobenzene in liquid ammonia<sup>198</sup>. Numbering of atoms is the one adopted throughout this chapter (see Figure 12).

	$a^N$	$a_2^H$	$a_3^H$	$a_4^H$	$a_5^H$	$a_6^H$
Nitro	11.46	3.42	1.11	3.89	1.11	3.42
Nitroso	7.97	3.84	0.96	2.97	1.14	4.14

Gulick and Geske<sup>199</sup> have synthesized nitrobenzene containing O<sup>17</sup> and have measured the O<sup>17</sup> isotropic coupling constant  $a^O$  of the corresponding anion radical. In acetonitrile they found a value for  $a^O$  of 8.86G. They considered the possibility of describing  $a^O$  by an analogous equation to the one used for  $a^N$ , namely

$$a^O = Q_1 \rho_O^\pi + Q_2 \rho_N^\pi$$

However, further experimental data seem to be necessary to determine the constants  $Q_1$  and  $Q_2$ .

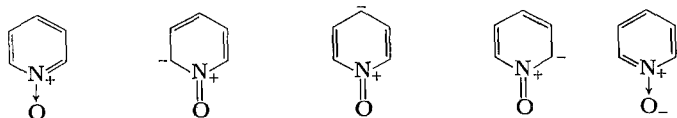
Ishitani and coworkers<sup>200</sup> have reported the electronic absorption spectrum of the anions of nitrobenzene and nitrotoluene. In the first case they report absorptions at 292 and 560 m $\mu$ , in the second case at 302, 607 and 875 m $\mu$ . An attempt is made to interpret the spectrum of the nitrobenzene anion by considering the coupling between a benzene negative ion and a nitro group and taking into account both locally excited and charge transfer configurations.

### C. Aromatic N-oxides and Nitroxides

#### I. The electronic structure of pyridine N-oxide and related compounds

The dipole moment of pyridine N-oxide is compared to that of trimethylamine oxide and *N,N*-dimethylaniline in Table 26. It appears that the dipole moment decreases as the polarizability of the

part of the molecule directly attached to the N—O bond increases. This may be visualized for pyridine *N*-oxide by the following resonance structures:



Whereas electrophilic substitution of pyridine is very difficult, the *N*-oxide readily forms the 2- and 4-nitro compounds. A comparison of the charge distributions in pyridine and pyridine *N*-oxide calculated by semiempirical SCF procedures<sup>201</sup> (type *b*) show a reversal of sign at the para position (see Figure 20). The oxygen atom contributes two electrons to the  $\pi$  system, resulting in a small  $\pi$  dipole moment opposite to the  $\sigma$  dipole moment. From the charge distribution shown in Figure 20 this reverse  $\pi$  moment is calculated to be 1.12 D, which is somewhat too large. Experimental evidence<sup>202</sup> (see also Table 26) and theoretical estimates by Kubota and Watanabe<sup>203</sup> point to a value of about 0.76 D for the  $\pi$  moment. This is not exactly the difference between the total dipole moments of

TABLE 26. Dipole moment of *N*-oxides, as given by reference 65.

	$\vec{\mu}_e$ (D)
$(\text{CH}_3)_3\text{N} \rightarrow \text{O}$	5.02
$(\text{CH}_3)_2\text{C}_6\text{H}_5\text{N} \rightarrow \text{O}$	4.79
$\text{C}_5\text{H}_5\text{N} \rightarrow \text{O}$	4.24

trimethylamine oxide and pyridine *N*-oxide, in view of the change in the state of hybridization of the nitrogen atom and the different numbers of C—N bonds. The dipole moments of 4-substituted pyridine *N*-oxides have been investigated by Katritzky and co-workers<sup>204</sup>.

It appears that in some cases pyridine *N*-oxide can also create a deficit of electrons at the 4-position, allowing for nucleophilic substitution.

Ito and Hata<sup>205</sup> and Jaffé<sup>206</sup> have reported the ultraviolet spectrum of pyridine *N*-oxide. The solvent dependence of the spectrum was further examined by Kubota and coworkers<sup>207,208</sup> correlated with data on other heterocyclic *N*-oxides and interpreted by semiempirical molecular orbital calculations (type *b*)<sup>203</sup>. These authors

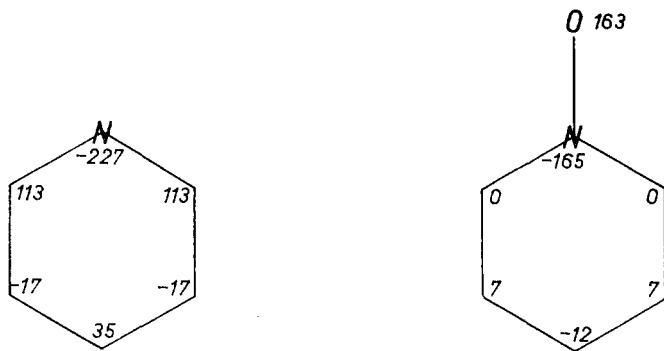


FIGURE 20. Ground state  $\pi$  electron distribution (in units of  $1/1000 |e|$ ) of pyridine and pyridine *N*-oxide<sup>201</sup>. Parameters adopted for these calculations are  $I_{N'} = 12.00$  eV,  $I_O' = 25.00$  eV,  $\beta_{CN} = -2.58$  eV,  $\gamma_{CN} = 7.58$  eV. Other parameters are as indicated in Table 14.

conclude that the  $282 \text{ m}\mu$  absorption (see Figure 21) in pyridine *N*-oxide is probably polarized parallel to the dipole moment and that it may be identified as a charge transfer band associated with a displacement of charge from the oxygen atom to the pyridine nucleus<sup>208</sup>. It should therefore not correspond to an enhanced  ${}^1L_b$  band of benzene (which would be polarized perpendicularly), as one might expect from the apparent analogy with the spectrum of pyridine.

The weaker  $317 \text{ m}\mu$  absorption measured in hexane has been interpreted as an  $n-\pi^*$  transition<sup>205,209</sup>. However, doubt has been cast on this assignment<sup>116,210</sup>, because of the strength ( $\epsilon > 1000$ ) of this band. In pyridine the  $n-\pi^*$  transition is locally weakly allowed. However, in pyridine *N*-oxide the nonbonding orbital on oxygen must be considered an almost pure  $2p_y$  orbital, making the  $n-\pi^*$  transition more strongly forbidden. Comparisons with calculations on pyridine show that the oxygen atom in pyridine *N*-oxide has the effect of shifting the  ${}^1L_b$  band to longer wavelength and of diminishing its intensity. In the author's opinion it therefore cannot be excluded that the  $317 \text{ m}\mu$  band of pyridine *N*-oxide actually contains the shifted and weakened  ${}^1L_b$  transition of pyridine which is polarized perpendicularly to the molecular axis.

Figure 21 shows the strong solvent dependence of the spectra of pyridine *N*-oxide and isoquinoline *N*-oxide. In water the first band of pyridine *N*-oxide appears at  $254 \text{ m}\mu$  and might be a superposition of the two  $317 \text{ m}\mu$  and  $282 \text{ m}\mu$  absorptions identified in *n*-hexane.



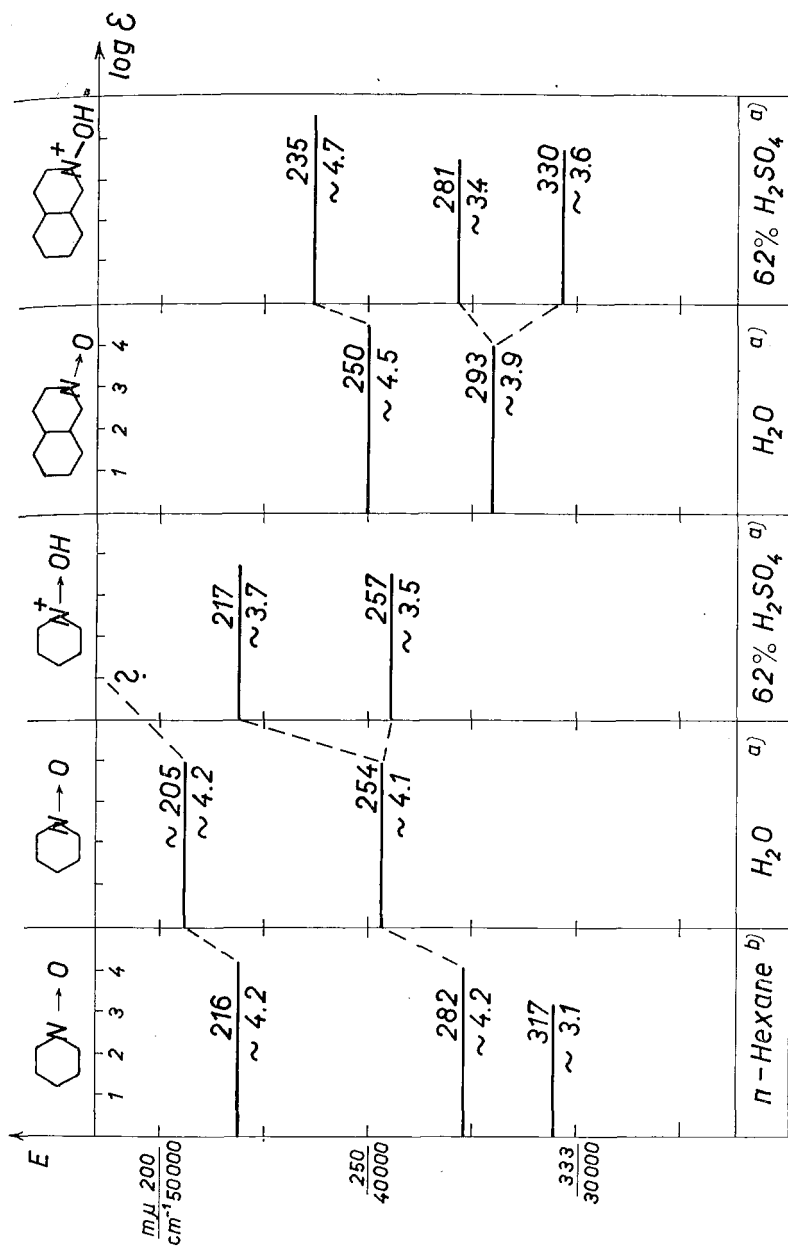


FIGURE 21. The solvent dependence of the longest-wavelength absorptions of pyridine N-oxide and isquinoline N-oxide. The data are from (a) reference 206, (b) reference 205 and 207.

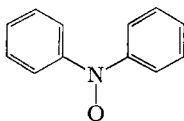
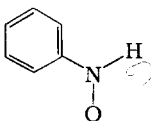
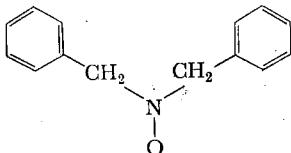
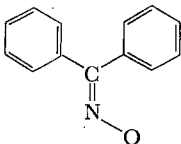
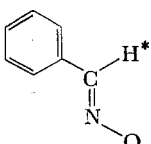
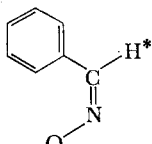
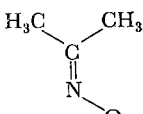
In strongly protonating medium this 254  $m\mu$  band seems to split up into two weaker bands as shown by Jaffé<sup>206</sup>. Investigations with protonating solvents have been carried out also by Kubota<sup>211</sup>.

The electronic spectrum of benzyldiene methylamine *N*-oxide is reported and interpreted theoretically by Kubota and Yamakawa<sup>212</sup>.

## 2. Magnetic properties of aromatic nitroxides

When the aminoxy-function enters into conjugation with a phenyl group, the unpaired electron becomes delocalized, thereby reducing the coupling constant  $a^N$ <sup>35, 213</sup>. On the other hand, in iminoxy radicals  $a^N$  is shown to be very insensitive to conjugation of the C—N—O system, confirming the  $\sigma$  character of the unpaired electron (see Table 27). In a large variety of iminoxy radicals,

TABLE 27. ESR data from reference 35 and 216. The assignment of the  $a^{H*}$  values to syn and anti benzaldoxime is based on more recent conclusions<sup>48, 214</sup>.

			
$a^N = 10.9$	$a^N = 11.9$	$a^N = 17.0$	
			
$a^N = 31.6$	syn $a^N = 31.6$ $a^{H^*} = 26.9$	anti $a^N = 29.2$ $a^{H^*} = 6.2$	$a^N = 33.0$

long-range couplings with protons are observed which are strongly dependent on the stereochemistry of the molecule<sup>214, 215</sup>. This stereochemical effect seems to have been first detected in the appearance of syn and anti isomers of benzaldoxime<sup>216</sup>. It is to be noted that the assignments of the syn and anti  $a^{H*}$  splitting constants in benzaldoxime as reported in reference 216 do not agree with the

theoretical conclusions by Berthier and coworkers<sup>48</sup> and represented by other investigators<sup>214, 215</sup>, according to which the unpaired-electron density should be larger on the H\* atom in the syn form (see Figure 6). Nonetheless, we find here the possibility for new and very promising applications of ESR spectroscopy to stereochemical problems.

#### IV. SOME SPECIAL TOPICS

##### A. Vibrational Spectra

Emphasis has been laid in this chapter on a description of the valence electrons in the molecules of interest and on physical properties which may be directly correlated with this description. From a more general point of view some physical aspects have unfortunately been neglected. One of these aspects, which is of great practical importance to the chemist, concerns the vibrations of the atomic nuclei in the molecules and their study by infrared and Raman spectroscopy. In view of the diversity of molecules considered here, it would be quite a task to give a unified theoretical treatment of the vibrational properties. As is well known, vibrations of polyatomic molecules must be described in terms of normal modes and cannot, strictly speaking, be localized within particular bonds. Nonetheless, it appears empirically that some particular vibrations may quite safely be ascribed to individual parts of a molecule, and that certain narrow ranges of IR frequencies are common to all molecules containing for instance C—N=O, or C—NO<sub>2</sub>, or  $\geq$ C—N → O bonds. We shall therefore indicate a few references where the interested reader may find some pertinent data and pursue this topic.

A general summary of IR data on nitroso and nitro compounds may be found in chapter 17 of the second edition of 'The Infra-red Spectra of Complex Molecules' by Bellamy<sup>217</sup>.

Mason<sup>22</sup> has described the vibrational fine-structure of the  $n-\pi^*$  band of trifluoronitrosomethane and has discussed NO stretching frequencies in both ground and excited electronic states. Nitromethane has more recently been studied between 4500 cm<sup>-1</sup> and 2000 cm<sup>-1</sup> by de Maine<sup>218</sup>. Jonathan<sup>219</sup> has investigated the vibrational spectrum of the aci-form of nitromethane in the region between 4000 cm<sup>-1</sup> and 450 cm<sup>-1</sup> and concludes that the C—N bond must have appreciable double bond character. This conclusion agrees with the picture obtained from the electronic spectrum (see section

II.C.2). Attempts have been made by the same author to correlate bond lengths and force constants with calculated bond orders for nitrogen-oxygen<sup>220</sup> and carbon-nitrogen<sup>219</sup> bonds.

A normal mode analysis of substituted benzene derivatives of symmetry  $C_{2v}$  has been carried out by Whiffen<sup>221</sup> and serves as a basis for the interpretation of the Raman spectrum and the IR spectrum of nitrobenzene between 4000 and  $285\text{ cm}^{-1}$ <sup>222</sup>.

A correlation of the intensities of the C—C and C—N ring stretching frequencies in pyridine and pyridine *N*-oxide with changes in the charge distribution due to substituents has been made by Katritzky<sup>223</sup>.

Some infrared data on the N—O stretching frequencies in stable nitroxides may be found in reference 42.

## B. Chemical Reactivity

The ultimate aim of theoretical chemistry unquestionably is the detailed understanding of chemical reactions. However, most reactions observed by the chemist proceed on a macroscopic scale and involve the interaction of a great number of atoms or molecules. The attempt to predict in detail the course of such a reaction mathematically is in some sense meaningless. Such a situation calls necessarily for a statistical interpretation. In particular cases reacting atoms and (or) molecules may individually be isolated from external influences—as for instance in a molecular beam experiment. The mathematical problem of interpreting such an experiment in reactive scattering on an *ab initio* basis is nevertheless already a formidable one.

Simple calculations on valence electrons, as have been described in this text, may at best serve as a basis for approximate descriptions of reactions. In this sense they may be considered as a refinement of the more conventional chemical formulae. Such interpretations are based on a conceptual model for the reaction in question. This involves the idea that if the reaction is to take place it must follow a certain well-defined path, or that it may choose between a limited number of possible paths, and that certain steps, or transition states, along the path are of decisive, rate-determining importance. The attempt is then made to assess the relative energy of possible transition states by simple quantum-chemical means.

Much work has been done in this sense on the reactivities of  $\pi$  electron systems, in particular on aromatic substitution, and the

main ideas and some results are to be found in basic texts<sup>224, 225</sup>, as in other more recent references<sup>226–228</sup>. The rate of aromatic substitution has been correlated with different theoretical quantities, such as  $\pi$  electron densities<sup>229</sup>, polarizabilities<sup>229</sup>, localization energies<sup>230</sup>, frontier electron densities<sup>231</sup> and superdelocalizabilities<sup>232</sup>, which may be estimated by semiempirical methods. However, these correlations must always be made with caution. An example to this point is given by nitrobenzene, which gets substituted mainly at the meta position by an electrophilic reagent. This fact is for instance not well reflected by the charge distribution given in Table 13 or Figure 12. The parameters used for this calculation have however been calibrated mainly on spectroscopic data and the aim of the calculation is to predict spectroscopic properties. The correlation between proneness to electrophilic attack and  $\pi$  electron density in nitrobenzene are better reflected by other calculations<sup>226</sup> which, in turn, are not primarily aimed at spectroscopic predictions. It is to be expected that the direct inclusion of  $\sigma$  electrons into semiempirical calculations will lead to a more complete picture of large molecules, also from the purely chemical point of view.

## V. ACKNOWLEDGMENT

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## CHAPTER 2

# Spectroscopy of the nitro group

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I. INTRODUCTION . . . . .	80
II. INFRARED AND RAMAN SPECTRA . . . . .	80
A. The $\nu_{as}$ and $\nu_s$ stretching frequencies . . . . .	82
1. Saturated nitro compounds . . . . .	82
2. Nitro olefins . . . . .	84
3. Aromatic and heterocyclic nitro compounds . . . . .	85
4. Other organic nitro compounds . . . . .	88
5. Salts of nitro compounds . . . . .	88
B. Other frequencies . . . . .	89
C. Infrared data on assorted nitro compounds and analysis . . . . .	90
D. Solvent effects . . . . .	91
III. ELECTRONIC ABSORPTION SPECTRA . . . . .	91
A. Nitroalkanes and nitro olefins . . . . .	92
B. Aromatic and heterocyclic nitro compounds . . . . .	94
C. Nitro derivatives and analysis . . . . .	102
D. Solvent effects . . . . .	103
E. Acid-base equilibria . . . . .	104
F. Ions . . . . .	105
IV. MICROWAVE SPECTRA . . . . .	106
V. NUCLEAR MAGNETIC RESONANCE SPECTRA . . . . .	106
VI. LITERATURE ON THE SPECTROSCOPIC DATA OF SOME ASSORTED NITRO COMPOUNDS . . . . .	111
VII. SPECTROSCOPIC STUDIES OF HYDROGEN BONDING AND KETO-ENOL EQUILIBRIA . . . . .	112

VIII. SPECTRA OF CHARGE TRANSFER COMPLEXES . . . . .	116
IX. ELECTRON SPIN RESONANCE SPECTRA . . . . .	120
X. MISCELLANEOUS SPECTROSCOPIC STUDIES . . . . .	125
XI. ACKNOWLEDGMENT . . . . .	125
XII. REFERENCES . . . . .	126

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## I. INTRODUCTION

Spectroscopic methods have been extensively employed for the study of organic nitro compounds and the literature abounds in publications where a variety of structural and analytical problems of interest to organic chemists have been investigated by spectroscopic techniques, particularly infrared and electronic absorption spectroscopy. Besides the applications of optical spectroscopy for the identification and characterization of nitro compounds, a large number of papers deals with environmental (substituent and solvent) effects, hydrogen bonding, enolization and acid-base equilibria. Nuclear magnetic resonance spectroscopy of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$  and  $^{15}\text{N}$  nuclei in nitro compounds have been examined. Electron spin resonance spectroscopy has been of immense value in the study of radical anions which are readily produced by the reduction of nitro compounds.

In this chapter, various aspects of the spectroscopy of organic nitro compounds will be reviewed in detail. In writing a review on a topic of this kind with innumerable references in the literature, it is possible that some of the workers have not been given proper credit due to over-sight or errors in judgment; the author would like to be excused for such omissions.

## II. INFRARED AND RAMAN SPECTRA

The infrared and Raman spectra of nitro compounds have been investigated in detail in the last few years. The important characteristic frequencies in the vibrational spectra of nitro compounds arise from the asymmetric ( $\nu_{\text{as}}$ ) and symmetric ( $\nu_{\text{s}}$ ) stretching vibration modes of the  $\text{NO}_2$  group. The vibrational assignments based on theoretical analysis as well as environmental effects on the nitro group frequencies have been discussed exhaustively in the literature.<sup>1-4</sup> In this section various aspects of the infrared and Raman spectra of the nitro compounds will be reviewed with particular emphasis on those aspects which are of interest to organic chemists.

TABLE 1. Fundamental frequencies for nitromethane<sup>5</sup>.

Vibrational class	Vibrational motion	Infrared (vapor) frequency $\text{cm}^{-1}$	Raman (liquid) $\text{cm}^{-1}$	Depolarization
$A_1$ (Totally symmetric)	$\text{NO}_2$ sym. stretching	1377	1377.3	0.2
	$\text{NO}_2$ sym. bending	658	656.5	0.39
	C—N Stretching	918	918.8	0.05
$A_2$	$\text{CH}_3$ twisting	Inactive	Inactive	—
$B_1$ (Parallel to $\text{NO}_2$ plane)	$\text{NO}_2$ asym. stretching	1586	1562	0.82
	$\text{NO}_2$ rocking	477	481	0.9
$B_2$ (Perpendicular to plane)	$\text{NO}_2$ rocking	605	608	—

The infrared spectra of nitro and nitroamine complexes of metals have been studied extensively. The  $\nu_{\text{as}}$ ,  $\nu_{\text{s}}$  and the wagging frequencies of the nitro group as well as the metal-nitrogen stretching frequencies have been reported; all these frequencies have been found to increase with the increase in the metal-nitrogen bond order. The nitro group frequencies in bridged nitro complexes and in stereoisomeric structures of certain complexes have been studied<sup>4</sup>.

TABLE 2. Vibrational frequencies of nitroparaffins<sup>5</sup>.

	$\text{CH}_3\text{NO}_2$ $\text{cm}^{-1}$	$\text{CD}_3\text{NO}_2$ $\text{cm}^{-1}$	$\text{C}_2\text{H}_5\text{NO}_2$ $\text{cm}^{-1}$	$(\text{CH}_3)_2\text{CHNO}_2$ $\text{cm}^{-1}$	$\text{C}_2\text{H}_5\text{CH}_2\text{NO}_2$ $\text{cm}^{-1}$
$\text{NO}_2$ sym. stretching	1377	1348	1366	1363	1385
C—N stretching	918	879	876	851	804
$\text{NO}_2$ sym. bending	658	632	621	630	610
$\text{NO}_2$ asym. stretching	1586	1571	1580	1575	1578
$\text{NO}_2$ rocking	477	424	—	—	—
$\text{NO}_2$ rocking	605	560	495 <sup>a</sup>	526	477 <sup>a</sup>

<sup>a</sup> measured in the liquid state.

The spectra of coordination compounds are, however, outside the scope of this review.

One of the early studies of the vibrational spectra of nitro compounds is by Nielsen and coworkers<sup>5</sup>, who examined the infrared and Raman spectra of four nitroparaffins. They could interpret all the fifteen fundamental frequencies of nitromethane satisfactorily and the important assignments are shown in Table 1. The correlations of the vibrational frequencies (in the vapor state) of nitroparaffins proposed by Nielsen and coworkers<sup>5</sup> are given in Table 2.

### A. The $\nu_{as}$ and $\nu_s$ stretching frequencies

#### I. Saturated nitro compounds

In alkyl nitro compounds the asymmetric ( $\nu_{as}$ ) and the symmetric ( $\nu_s$ ) stretching frequencies of the nitro group are found in the region 1500–1600 and 1300–1370  $\text{cm}^{-1}$ , respectively<sup>1-3</sup>. The  $\nu_{as}$  and  $\nu_s$  in a few aliphatic nitro compounds are given in Table 3. Generally, primary and secondary nitro compounds absorb at slightly higher frequencies than tertiary compounds<sup>6</sup>. Environmental effects on the  $\nu_{as}$  and  $\nu_s$  are quite marked.  $\alpha$ -Halogen substituents increase the stretching frequency considerably; thus,  $\nu_{as}$  in  $\text{CF}_3\text{NO}_2$  and  $\text{CCl}_3\text{NO}_2$  are 1607 and 1610  $\text{cm}^{-1}$ , respectively<sup>7</sup>. In *gem*-dinitro compounds  $\nu_{as}$  and  $\nu_s$  are

TABLE 3. The  $\text{NO}_2$  stretching frequencies (in  $\text{cm}^{-1}$ ) in aliphatic nitro compounds<sup>11</sup>.

$\text{RNO}_2$			$\text{R}(\text{CH}_3)_2\text{CNO}_2$		
<i>R</i>	$\nu_{as}$	$\nu_s$	<i>R</i>	$\nu_{as}$	$\nu_s$
$\text{C}_2\text{H}_5\text{CHCH}_3$	1548	1359	$\text{CH}_3\text{CH}_2$	1534	1351
$(\text{CH}_3)_2\text{CH}$	1553	1359	$\text{CH}_3$	1541	1345
$\text{CH}_3(\text{CH}_2)_3$	1550	1379	H	1553	1359
$\text{CH}_3(\text{CH}_2)_2$	1553	1385	$\text{CH}_3\text{CH}(\text{OH})$	1543	1353
$\text{CH}_3\text{CH}_2$	1550	1368	$\text{HOCH}_2$	1543	1353
Cyclo $\text{C}_6\text{H}_{11}\text{CH}_2$	1553	1383	Cl	1565	1341
$\text{CH}_3$	1567	1379	$\text{O}_2\text{N}$	1572	1330
$\text{C}_2\text{H}_5\text{CH}(\text{OCH}_3)\text{CH}_2$	1550	1379			
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2$	1555	1370			
$\text{C}_6\text{H}_5\text{CH}_2$	1556	1375			
$\text{C}_2\text{H}_5\text{OOCCHCH}_2\text{C}_2\text{H}_5$	1560	1368			
$\text{C}_2\text{H}_5\text{CHCl}$	1570	1340			
$\text{CH}_3\text{CCl}_2$	1587	1325			
$\text{CF}_3$	1607	1311			
$\text{CCl}_3$	1610	1307			

found near 1580 and 1330  $\text{cm}^{-1}$ , respectively<sup>8</sup>. Similar effects are found in the presence of a carbethoxy group in the  $\alpha$ -position<sup>9</sup>. The nitro group has surprisingly little effect on the positions of  $\text{C}=\text{C}$  or  $\text{C}-\text{H}$  stretching bands in nitro olefins. In  $\alpha$ -nitroketones, however, both the carbonyl and the  $\nu_{\text{as}}$  frequencies are shifted to higher frequencies.

Brown<sup>8</sup> first attempted to find a correlation between the  $\nu_{\text{as}}$  and the  $\nu_{\text{s}}$  in aliphatic nitro compounds; there was little success probably because of the presence of coupling between the  $\text{C}-\text{N}$  stretching and the  $\nu_{\text{as}}$  modes. Bellamy and Williams<sup>10</sup> consider this failure to be due to dipole and steric effects; this suggestion is, however, not consistent with the low barrier of rotation found in nitromethane. Lunn<sup>11</sup> has recently examined the correlation between the  $\nu_{\text{as}}$  and the  $\nu_{\text{s}}$  frequencies in a large number of aliphatic nitro compounds and finds the following relations:

$$\nu_{\text{sym}} = 3262 - 1.213 \nu_{\text{asym}} \text{ for } \text{RNO}_2$$

$$\nu_{\text{sym}} = 2310 - 0.622 \nu_{\text{asym}} \text{ for } \text{R}(\text{CH}_3)_2\text{CNO}_2$$

Correlation coefficients for the above two relations were 0.940 and 0.856, respectively.

Several workers<sup>6,12</sup> have attempted to correlate the nitro group stretching frequencies in aliphatic derivatives with substituent constants<sup>11,13,14</sup>. Rao and Venkataraghavan<sup>14</sup> have proposed the relation,

$$\nu_{\text{as}} = 25.1\sigma^* + 1557$$

for compounds of the type  $\text{RNO}_2$ . The  $\sigma^*$  constants are the aliphatic polar substituent constants of Taft. The correlation included data on seven compounds and the correlation coefficient was 0.99. Lunn<sup>11</sup> has examined the data on 29 compounds of the type  $\text{RNO}_2$  and has proposed the relation,

$$\nu_{\text{as}} = 21.37\sigma^* + 1550.7$$

the correlation coefficient being about 0.987. A similar correlation has been proposed for compounds of the formula  $\text{R}(\text{CH}_3)_2\text{CNO}_2$ , with a coefficient of 0.981.

$$\nu_{\text{as}} = 23.92\sigma^* + 1538.5$$

It must be mentioned that these correlations do not include compounds where a halogen atom is directly attached to the nitro group. Taft's  $\sigma^*$  constants can describe the polar effects of the substituents on the nitro group frequencies only when the halogens are attached



to the carbon atom as in  $\text{CCl}_3\text{NO}_2$  or  $\text{CF}_3\text{NO}_2$ ; however, when the halogen is directly attached to the nitrogen atom, non-bonded effects become important.

Halmann and Pinchas<sup>15</sup> have studied the infrared spectrum of  $^{18}\text{O}$  substituted nitromethane and find  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  at 1525 and 1357  $\text{cm}^{-1}$ , respectively. The intensity of the symmetric stretching band of nitromethane has been found to be  $0.63 \times 10^4 \text{ mole}^{-1} \text{ l. cm}^{-2}$ ; this intensity is three times that of the symmetric deformation band and 18 times that of the C—N stretching band<sup>16</sup>. The measured intensities have been related to dipole moments and as well as to the derivatives of the dipole moment with respect to bond lengths. Similar studies have also been carried out by Popov and Shlyapochnikov<sup>17</sup> who report the bond moments in  $\text{CH}_3\text{NO}_2$  to be:  $\mu_{\text{NO}} = 1.5$ ,  $\mu_{\text{CN}} = 1.8$ , and  $\mu_{\text{CH}} = 0.3$  debyes. The thermodynamic properties of  $\text{CCl}_3\text{NO}_2$  have been calculated on the basis of vibrational spectra by Castelli and Pristera<sup>18</sup>. The analysis of the infrared and Raman vibrational spectra of a number of nitroalkanes and polynitroalkanes have been carried out by Popov and Shlyapochnikov<sup>19</sup> and by Geiseler and Kessler<sup>20</sup>. Infrared and Raman assignments have been made for *gem*-dinitropropane<sup>21</sup>. The infrared spectra of O-ethyl ethers of dinitro- and trinitromethanes have been studied<sup>22</sup>. The  $\nu_{\text{s}}$  band shows splitting in aliphatic nitro compounds containing the

$\begin{array}{c} | \\ \text{R}-\text{C}-\text{NO}_2 \\ | \end{array}$

group with  $\text{R} = \text{CH}_3$  or  $\text{NO}_2$ <sup>23</sup>. The infrared spectra of aliphatic  $\beta$ -nitroalcohols show  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  bands in the ranges 1550–1580 and 1350–1380  $\text{cm}^{-1}$ , respectively<sup>24</sup>.

## 2. Nitro olefins

Conjugation of a nitro group with a double bond lowers the stretching frequencies of the nitro group<sup>25</sup>. For example, 2-methyl-1-nitropropene shows the bands at 1515 and 1350  $\text{cm}^{-1}$  while 2-methyl-3-nitropropene absorbs at 1555 and 1366  $\text{cm}^{-1}$ . For monoalkyl nitroethylenes the ranges  $1524 \pm 4$  and  $1353 \pm 6 \text{ cm}^{-1}$  have been quoted<sup>8</sup>. Yamashita and Namba<sup>26</sup> quote  $1519 \pm 6$  and  $1347 \pm 5 \text{ cm}^{-1}$  for  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  of nitro olefins. For di- and trialkylnitroethylenes the ranges are  $1515 \pm 4$  and  $1346 \pm 9 \text{ cm}^{-1}$ . Raman data on nitrodiene have been reported<sup>27</sup>. The intensity of  $\nu_{\text{s}}$  is increased greatly on conjugation while the intensity of  $\nu_{\text{as}}$  does not seem to vary markedly<sup>28</sup>.

### 3. Aromatic and heterocyclic nitro compounds

Vibrational spectra of aromatic nitro compounds have been investigated by a number of workers and of these special mention must be made of the early work of Brown<sup>8</sup>, Francel<sup>29</sup>, Randle and Whiffen<sup>30</sup>, and Kross and Fassel<sup>31</sup>. Coplanar aromatic nitro groups

TABLE 4. The NO<sub>2</sub> stretching frequencies (in cm<sup>-1</sup>) in aromatic nitro compounds<sup>31,34</sup>.

Compound	$\nu_{as}$ (solid)	$\nu_s$ (solid)	Compound	$\nu_{as}$ (solid)	$\nu_s$ (solid)
Sodium					
<i>p</i> -nitrophenoxide	1501	1338	<i>p</i> -Nitrobromobenzene	1532	1345
<i>p</i> -Nitrodiphenylamine	1526	1324	<i>p,p'</i> -Dinitroazoxy- benzene	1528	1343
<i>p</i> -Nitroaniline	1504	1333	<i>p</i> -Nitromethylaniline	1532	1315
<i>p,p'</i> -Dinitrodiphenyl- sulfide	1511	1337	<i>p</i> -Nitrobenzaldehyde	1533	1343
<i>p</i> -Nitrophenol	1515	1342	<i>p</i> -Nitrobenzoic acid	1541	1351
			<i>p</i> -Dinitrobenzene	1553	1344
<i>p</i> -Nitroanisole	1517	1342	<i>m</i> -Nitrotoluene	1537	1350
<i>p,p'</i> -Dinitrodiphenyl	1514	1340	<i>m</i> -Nitroaniline	1522	1345
<i>p</i> -Nitrophenylacetic acid	1515	1342	<i>m</i> -Nitroacetanilide	1539	1346
<i>p</i> -Nitroacetanilide	1515	1335	<i>o</i> -Nitroaniline	1513	1349
<i>p</i> -Nitrotoluene	1517	1344	<i>o</i> -Nitroacetanilide	1500	1341
<i>p</i> -Nitrodiphenyl	1510	1342	<i>o</i> -Nitrotoluene	1530	1349
<i>p</i> -Nitrodimethylaniline	1522	1316	<i>o</i> -Nitrobiphenyl	1534	1360
<i>p</i> -Nitrobenzonitrile	1524	1348	<i>o</i> -Nitrobenzaldehyde	1536	1348
<i>p</i> -Nitrochlorobenzene	1526	1343	<i>o</i> -Trifluoromethyl- nitrobenzene	1539	1359
<i>p</i> -Nitroiodobenzene	1513	1345	<i>o</i> -Ethylnitrobenzene	1531	1352

generally exhibit  $\nu_{as}$  in the range 1520–1550 cm<sup>-1</sup>. Presence of strongly electron withdrawing groups in the *para*-position or bulky groups in the *ortho*-position tend to increase the  $\nu_{as}$  (1540–1570 cm<sup>-1</sup>). Electron donating groups lower the  $\nu_{as}$  (1490–1525 cm<sup>-1</sup>). The position of  $\nu_{as}$  and  $\nu_s$  in a few aromatic nitro compounds are summarized in Table 4. A plot of  $\nu_{as}$  against  $\nu_s$  does not give a continuous curve; the deviations are particular great in the presence of electron withdrawing groups in the *para*-position<sup>31</sup>. Apparently, in such cases the C—N bond order is decreased while the N—O bond order is increased at the same time, thus maintaining a roughly constant value of  $\nu_s$ .

In substituted nitrobenzenes  $\nu_{as}$  and  $\nu_s$  have been correlated with structure related parameters such as molecular dipole moments and Hammett  $\sigma$  constants<sup>14,31</sup>. The linear correlation of  $\nu_{as}$  with the  $\sigma$  and  $\sigma^+$  substituent constants as proposed by Rao and Venkataraghavan<sup>14</sup> are:

$$\nu_{as} = 305\sigma + 1523 \text{ (correlation coefficient 0.961)}$$

$$\nu_{as} = 19.2\sigma^+ + 1528 \text{ (correlation coefficient 0.934)}$$

Contrary to these findings, Hamer and coworkers<sup>32</sup> have recently reported the absence of a good linear relation between  $\nu_{as}$  and Hammett's  $\sigma$  constant in some *meta*- and *para*-disubstituted benzene derivatives. On the other hand,  $\nu_{as}$  and  $\nu_s$  of 4-substituted 2-nitroanilines show linear relations with the  $\sigma$  constants<sup>33</sup>.

In aromatic compounds containing two or more nitro groups, multiple frequencies are observed. Doubling of the stretching frequency has been noticed by Bellamy<sup>1</sup> and Conduit<sup>34</sup> in compounds where one nitro group is coplanar and another is twisted out of plane.

The stretching bands of the nitro group are quite intense, but the absolute intensities vary markedly from compound to compound. It is therefore not possible to estimate the number of nitro groups by employing these bands. Generally, the asymmetric stretching band is much more intense than the symmetric band. Considerable variations in band shapes are often noticed in compounds where there is steric hindrance.

The integrated intensities of  $\nu_{as}$  and  $\nu_s$  bands in nitrobenzene were found to be  $2.72 \times 10^4$  and  $1.86 \times 10^4$  l. mole<sup>-1</sup> cm<sup>-2</sup> respectively<sup>34</sup>; intensity data on other aromatic nitro compounds have also been given by Conduit. The molar extinction coefficients, half-band widths as well as integrated intensities of  $\nu_{as}$  and  $\nu_s$  bands in several aromatic compounds have been given by Flett<sup>35</sup>. Some of the data are summarized in Table 5.

The half-band widths and band intensities of  $\nu_{as}$  and  $\nu_s$  bands of 4-substituted 2-nitroanilines have been correlated with the Hammett  $\sigma$  constants of substituents<sup>33</sup>. Raman intensities of the nitro group stretching vibrations of a number of *para*- and *meta*-substituted benzene derivatives have also been correlated with the Hammett  $\sigma$  constants<sup>36</sup>.

The infrared spectrum of <sup>18</sup>O labelled nitrobenzene has been examined and the assignments have been discussed in detail<sup>37</sup>.

TABLE 5. Half-band widths and intensities of  $\nu_{as}$  and  $\nu_s$  bands in aromatic nitro compounds<sup>a</sup>

Compound	$\nu_{as}$	$\Delta\nu_{1/2}$	$\epsilon_{max}$	$B \times 10^{-2}$	$\nu_s$	$\Delta\nu_{1/2}$	$\epsilon_{max}$	$B \times 10^{-2}$
<i>p</i> -Chloronitrobenzene	1523	15.3	403	71.0	1347	9.6	394	52.8
<i>m</i> -Carbethoxynitrobenzene	1536	11.1	484	65.0	1355	6.3	760	55.0
<i>p</i> -Cyanonitrobenzene	1534	12.0	572	71.7	1353	7.7	542	50.5
<i>p</i> -Methoxynitrobenzene	1506	13.3	368	71.2	1340	14.5	476	96.6
<i>p</i> -Nitrobenzamide	1519	11.8	372	48.5	1346	15.3	464	92.5
<i>p</i> -Nitrobenzoic acid	1547	6.2	279	46.0	1354	10.6	302	42.7
<i>p</i> -Carbomethoxynitrobenzene	1531	10.9	705	85.0	1351	9.9	392	54.3
<i>p</i> -Nitrobenzene-sulphonic acid	1540	8.6	488	44.3	1354	5.6	690	49.4
<i>m</i> -Cyanonitrobenzene	1541	10.2	537	67.6	1360	7.6	560	64.2
<i>p</i> -Dimethylamino-nitrobenzene	1492	15.0	204	36.6	1324	31.3	1153	36.0
<i>m</i> -Dinitrobenzene	1545	—	288	80.8	1352	12.6	352	55.2
<i>p</i> -Nitrodiphenyl	1520	7.5	572	56.3	1350	10.1	765	77.6

<sup>a</sup>  $\Delta\nu_{1/2}$  in  $\text{cm}^{-1}$ ;  $\epsilon_{max}$  in liter mole<sup>-1</sup>  $\text{cm}^{-1}$ ;  $B$  in practical units (multiplication by  $1.15 \times 10^{-10}$  gives absolute units).

<sup>18</sup>O-Nitrobenzene shows  $\nu_{as}$  and  $\nu_s$  bands at 1510 and 1322  $\text{cm}^{-1}$ , respectively, compared to <sup>16</sup>O-nitrobenzene which shows these bands at 1531 and 1349  $\text{cm}^{-1}$ . The <sup>15</sup>N-nitrobenzene spectrum has also been reported<sup>38</sup> and the  $\nu_{as}$  and  $\nu_s$  bands are found at 1501 and 1327  $\text{cm}^{-1}$ , respectively.

Recently, the dichroism of oriented crystals of several aromatic nitro compounds has been studied<sup>39</sup> and various assignments and correlations have been discussed. 9-Nitroanthracene is found to be deformed from the planar configuration due to steric hindrance. Assignments of fluoronitrobenzenes have been examined in some detail by Medhi<sup>40</sup>. Infrared spectra of a number of alkylnitrobenzenes have been studied by Kinugasa and coworkers<sup>41</sup> with particular reference to the intensities of  $\nu_{as}$  and  $\nu_s$  bands as well as the substituent effects on the frequencies. Alkyl substituents in 2- or 2,6-positions cause higher  $\nu_{as}$  frequencies due to steric effects. The infrared spectrum of 2,3,5,6-tetra-*iso*-propyl-1-nitrobenzene has been explained in terms of steric effects which are shown to be higher than in nitrodurene<sup>42</sup>. The intensity of  $\nu_s$  is lowered by ortho substituents<sup>43</sup>. A linear relation between  $\nu_{as}$  and dipole moments of aromatic nitro compounds has been proposed by Kinugasa and

Nakashima<sup>41</sup>; different linear relations are found for halonitrobenzenes and alkylnitrobenzenes. The effect of conjugative interaction between the nitro group and sulphur containing substituents on  $\nu_{as}$  has been studied and a linear relationship between  $\nu_{as}$  and Brown's  $\sigma^+$  constants has been reported<sup>44</sup>. The effects of *para*-CH<sub>2</sub>X (where X is any substituent) groups on the vibrational frequencies of the nitro group have been examined by Borek<sup>45</sup>.

The positions of  $\nu_{as}$  and  $\nu_s$  bands of the nitro group in heterocyclic compounds have been related to their electron donating character<sup>46a</sup>. The nitro group stretching absorption occurs at higher frequencies as the ring becomes more and more electron-attracting in nature. It has been observed that the 2-thienyl ring is a strong electron donor. Pyridine-1-oxide donates electrons readily from the 4-position but not from the 3-position. The pyridine ring is a weak donor both at the 2- and 4-positions<sup>46a</sup>. The extinction coefficients of the  $\nu_{as}$  and  $\nu_s$  bands in heterocyclic derivatives have been reported along with some data on nitrobenzenes. The apparent extinction coefficient of the  $\nu_{as}$  band in azanaphthalene permits the distinction between  $\alpha$ - and  $\beta$ -substituents<sup>46b</sup>. Raman intensities of nitro group bands in 5-nitrofurane derivatives have been discussed in terms of intramolecular interactions<sup>47</sup>.

#### 4. Other organic nitro compounds

Nitroamines and other *N*-nitro compounds exhibit  $\nu_{as}$  and  $\nu_s$  frequencies generally in the ranges 1530–1660 and 1250–1320 cm<sup>-1</sup>, respectively. Nitroamines, polynitroamines, nitroguanidines, nitroureas, and other *N*-nitro compounds also absorb within these ranges<sup>1,48</sup>. Infrared spectra of  $\alpha$ -nitroketones have been examined by Simmons and coworkers<sup>49</sup>. Based on the infrared spectra of *N*-nitroamides and *N*-nitrocarbamates, evidence has been presented for the existence of rotational isomers in the latter compounds<sup>50</sup>. The doubling of the  $\nu_{as}$  band in the nitrocarbamates is attributed to the strong interaction between the nitro group and the two different oxygen atoms of the carbomethoxy group. *N*-nitroamides exist largely in the transoid conformation<sup>50</sup>.

Covalent nitrates show  $\nu_{as}$  and  $\nu_s$  bands of the nitro group in the regions 1600–1650 and 1250–1300 cm<sup>-1</sup><sup>1,8,48</sup>.

#### 5. Salts of nitro compounds

Infrared spectra of sodium salts of a few nitroalkanes have been studied<sup>51,52</sup> and the  $\nu_{as}$  and  $\nu_s$  frequencies of the carbonitronate ion

have been assigned to the regions 1200–1320 and 1040–1175  $\text{cm}^{-1}$ , respectively. The C=N frequency in these salts appears in the region 1585–1605  $\text{cm}^{-1}$ . The infrared spectra of the nitromethane anion has been studied in detail by Yarwood and Thomas<sup>53</sup> who have proposed a structure in which an atomic dipole is associated with the carbon atom. The assignments of  $\nu_{\text{as}}$  ( $\sim 1575 \text{ cm}^{-1}$ ) and  $\nu_{\text{s}}$  ( $\sim 1270 \text{ cm}^{-1}$ ) by these authors differs from other authors. The carbonyl and nitrile stretching frequencies in  $\alpha$ -nitroketones and  $\alpha$ -nitronitriles are considerably reduced in the salts due to the conjugative effect of the carbonitronate group<sup>52</sup>. Infrared spectra of several salts of 1,1-dinitroalkanes and trinitromethane have been examined<sup>54–56</sup>. Kaplan<sup>55</sup> assigns the  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  bands around 1260 and 1170  $\text{cm}^{-1}$ , respectively, while Kamlet and coworkers<sup>56</sup> assign these frequencies in the region 1480 and 1250  $\text{cm}^{-1}$ , respectively. A relationship in salts of nitro compounds between the  $\nu_{\text{s}}$  and the C—N bond order has been proposed<sup>56</sup>.

### B. Other frequencies of nitro compounds

The C—N stretching vibration frequency in nitromethane has been assigned<sup>5</sup> to a band at  $\sim 920 \text{ cm}^{-1}$ . In other aliphatic nitro compounds a band in the region 830–920  $\text{cm}^{-1}$  is found due to the C—N stretching vibration. In aromatic nitro compounds<sup>1,2</sup>, the C—N stretching absorption has been assigned to a band at  $\sim 850 \text{ cm}^{-1}$ . It should be pointed out that the assignment of the C—N stretching bands in nitro compounds is uncertain<sup>8,31</sup>. Kross and Fassel<sup>31</sup> have preferred to assign the band at  $\sim 1300 \text{ cm}^{-1}$  in aromatic nitro compounds to the C—N stretching vibration; the assignment seems to be reasonable. The C—N stretching frequency should be expected to vary due to the wide variation in the bond order depending upon substitution and other factors. From the study of the spectrum of  $^{18}\text{O}$ -nitrobenzene, Pinchas and coworkers<sup>37</sup> have assigned a band at  $\sim 1105 \text{ cm}^{-1}$  to the C—N stretching vibration. The C—N stretching frequency in halonitrobenzenes has been assigned recently<sup>57</sup> to a band around 1260  $\text{cm}^{-1}$ .

Nitro compounds show other low frequency bands due to skeletal and deformation vibrations. In nitromethane, a band at  $\sim 660 \text{ cm}^{-1}$  was assigned to the symmetric bending vibration while bands at  $\sim 475$  and  $\sim 605 \text{ cm}^{-1}$  were ascribed to the rocking vibrations of the nitro group<sup>5</sup>. In nitrobenzene, bands at  $\sim 850$ ,  $\sim 530$ , and  $\sim 420 \text{ cm}^{-1}$  have been assigned to the symmetric  $\text{NO}_2$  deformation, the out-of-plane  $\text{NO}_2$  bending and the in-plane  $\text{NO}_2$  rocking

vibrations, respectively<sup>37</sup>. In a number of meta- and para-substituted nitrobenzenes, the symmetric deformation, the in-plane, and the out-of-plane rocking vibrations have been assigned to the bands at  $\sim 860$ ,  $\sim 530$ , and  $730\text{ cm}^{-1}$ , respectively<sup>58</sup>.

In nitroamines and in certain *N*-nitro compounds, a band of medium intensity is found at  $\sim 780\text{ cm}^{-1}$ , possibly arising from a deformation vibration<sup>1,48</sup>. In the salts of nitro compounds, a band around  $750\text{ cm}^{-1}$  is seen due to the bending vibration<sup>52,56</sup>. Yarwood and Thomas<sup>53</sup> have assigned bands at 735, 680, and  $536\text{ cm}^{-1}$  for the three deformation modes in sodium methanenitronate.

In alkyl nitro compounds, a band at  $\sim 1379\text{ cm}^{-1}$  has been observed even in the absence of a methyl group<sup>6</sup>. This has been assigned to the perturbed methylene group in these compounds<sup>1</sup>. Similar additional bands have been seen in secondary alkyl nitro compounds<sup>8</sup>.

### C. Infrared data on assorted nitro compounds and analysis

In the recent literature, innumerable references are found regarding infrared data of nitro derivatives. A few of the recent references include, derivatives of 1,3-dinitrobenzene and 1,3,5-trinitrobenzene<sup>59</sup>, 4-halo derivatives of 1-nitronaphthalene<sup>60</sup>, nitrated derivatives of 4-benzoylnaphthalic anhydride<sup>61</sup>, dinitroacetonitrile and its salts<sup>62</sup>, nitroacridine and its derivatives<sup>63</sup>, *p*-nitrobenzyl esters of carboxylic acids<sup>64</sup>, dinitrophenyl derivatives of amino acids<sup>65</sup>, nitro derivatives of dioxaboracyclohexane<sup>66</sup>, 2-nitroindenedione derivatives<sup>67</sup> and nitrocellulose.<sup>68</sup> References where infrared and other spectral data are summarized will be referred to later.

Infrared spectroscopy has been used for quantitative analysis in several instances and some of the recent papers deal with 3,5-dinitrobenzoate esters of hydroxylic compounds<sup>69</sup>, location of ester groups in cellulose nitrates<sup>70</sup> and determination of aldehydes and ketones as DNPH derivatives<sup>71,72</sup>.

The paths and the products of many organic reactions involving nitro compounds have been studied employing infrared spectroscopy: isomerization of 1-nitro-2-propene<sup>73</sup>, Michael reaction with *gem*-dinitroalkyl  $\alpha,\beta$ -unsaturated esters and other substrates with nitroalkanes<sup>74</sup>, nitration of barene<sup>75</sup>, polymerization of nitro olefins<sup>76</sup>, action of nitrous vapors on anthracene<sup>77</sup>, and preparation of 2-bromo-2-nitroalkyl amines<sup>78</sup>.

### D. Solvent effects

The infrared spectra of nitromethane recorded as a neat liquid as well as in carbon tetrachloride solutions at various concentrations showed negligible frequency shifts<sup>79</sup>. The molar extinction coefficient of the band at  $3040\text{ cm}^{-1}$  decreases with the concentration of nitromethane, suggesting specific interaction between two nitromethane molecules<sup>80</sup>. Influence of solvents on the frequency and intensity of nitro group vibrations in a number of nitro compounds has been found to be negligible in the absence of hydrogen bonding<sup>81</sup>. The intensities of the absorption bands of *p*-substituted nitrobenzenes have been found to decrease with the polarity of the solvent<sup>82</sup>. The influence of solvents on the infrared spectra of dinitrotoluenes has been reported<sup>83</sup>.

## III. ELECTRONIC ABSORPTION SPECTRA

In simple nitro compounds like nitromethane, the nitrogen makes use of three  $sp^2$  hybridized orbitals for bonding and an unshared electron pair ( $p\pi$  orbital) remains on the nitrogen. The oxygen atoms also have one  $p\pi$  electron each, besides two unshared pairs of electrons in the plane of the nitro group. The energy level diagram of the nitro group is shown in Figure 1. The symmetric and anti-symmetric combinations of the nitrogen orbitals ( $n_s$  and  $n_a$ ) would give rise to two  $n \rightarrow \pi^*$  transitions<sup>84,85</sup>.

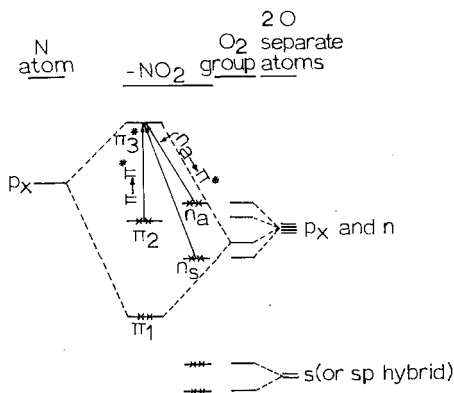


FIGURE 1. Energy level diagram of the nitro group<sup>84</sup>



### A. Nitroalkanes and nitro olefins

Nitromethane exhibits two absorption bands at  $270\text{ m}\mu$  ( $\log \epsilon\ 1.3$ ) and  $210\text{ m}\mu$  ( $\log \epsilon\ 4.2$ ). The lowest energy bands of an aliphatic nitrate, a nitrite, and a nitro compound are compared in Figure 2.

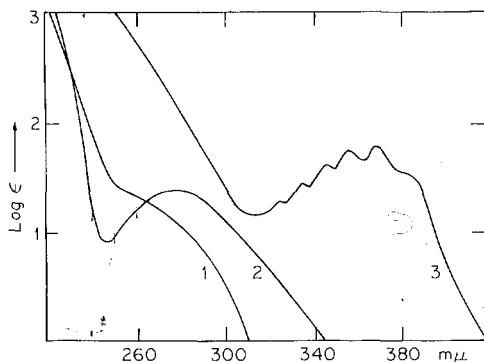


FIGURE 2. The  $n \rightarrow \pi^*$  transition bands of (1) 2-butylnitrate in ethanol, (2) 2-nitrobutane in ethanol and (3) 2-butylnitrite in ether<sup>86</sup>.

The weak band at  $270\text{ m}\mu$  does not show fine structure even in non-polar solvents, but is shifted to lower wavelengths with the increasing polarity (or proton-donating ability) of the solvent typical of an  $n \rightarrow \pi^*$  transition<sup>85</sup> (Figure 3). The  $270\text{ m}\mu$  band is undoubtedly due to the  $n_a \rightarrow \pi_3^*$  transition<sup>84</sup>, while the  $210\text{ m}\mu$  absorption is due to the  $\pi_2 \rightarrow \pi_3^*$  transition. Nagakura<sup>86b</sup> has assigned these bands at  $270$  and  $200\text{ m}\mu$  in the vapor phase. There should be another band at much lower wavelengths (in the vacuum ultraviolet region) due to  $n_s \rightarrow \pi_3^*$  transition, but this band has not been reported.

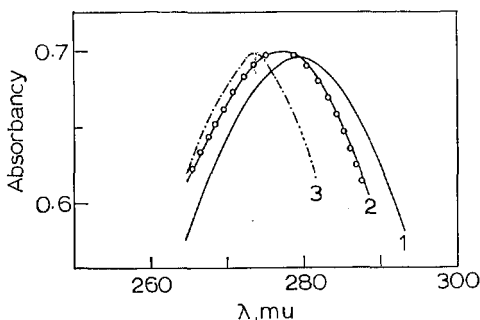


FIGURE 3. Solvent effects on the  $n \rightarrow \pi^*$  transition band of nitromethane; (1) in heptane (2) in methanol and (3) in water.

It can be seen from Table 6 that there is considerable effect of substituents on the position of the  $n \rightarrow \pi^*$  transition band. The effect of the alkyl substituents can not be simply correlated with Taft's aliphatic polar substituent constants ( $\sigma^*$ ). Balasubramanian and Rao<sup>87</sup> have been able to correlate the  $n \rightarrow \pi^*$  frequencies with the  $\sigma^*$  constants after accounting for the contributions from the C—H and the C—C hyperconjugation of the alkyl groups. In

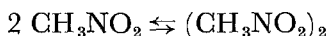
TABLE 6. Long-wavelength  $n \rightarrow \pi^*$  bands of aliphatic nitro compounds ( $\text{RNO}_2$ )<sup>85,87</sup>.

R	Heptane		Methanol <sup>a</sup>	Water <sup>a</sup>
	$\lambda_{\text{max}}$ , m $\mu$	$\epsilon_{\text{max}}$	$\lambda_{\text{max}}$ , m $\mu$	$\lambda_{\text{max}}$ , m $\mu$
$\text{CH}_3$	275	14.5	271.5	268.5
$\text{C}_2\text{H}_5$	277	19.8	274	270.5
<i>i</i> - $\text{C}_3\text{H}_7$	279.5	21.4	277	273.5
<i>t</i> - $\text{C}_4\text{H}_9$	280.5	22.5	279	275
$\text{CF}_3$	279	52	—	—
$\text{CCl}_3$	278.5	—	—	—

<sup>a</sup> The  $\epsilon_{\text{max}}$  values are of the same magnitude as in heptane.

Figure 4, the  $n \rightarrow \pi^*$  frequencies of the aliphatic nitro compounds have been plotted against the Taft  $\sigma^*$  constants with and without the correction for the hyperconjugative contribution,  $(n_{\text{H}}h_{\text{H}} + n_{\text{C}}h_{\text{C}})$ , where  $n$  stands for the number of  $\alpha$ -hydrogens or carbons available for hyperconjugation and  $h$  stands for the hyperconjugation constant. The  $h_{\text{H}}$  and  $h_{\text{C}}$  have been found to be  $\sim 550$  and  $\sim 360 \text{ cm}^{-1}$ , respectively. The linear correlation in Figure 4(b), has been taken as evidence for the existence of hyperconjugation in electronically excited states of molecules. Further, the  $n \rightarrow \pi^*$  frequencies in alkyl nitro compounds follow the Baker-Nathan order ( $\text{Me} > \text{Et} > i\text{-Pr} > t\text{-Bu}$ ). This trend is maintained in solvents of varying degree of polarity and/or proton donating ability<sup>87</sup>.

From a detailed study of the ultraviolet absorption spectra of nitromethane in a variety of solvents, de Maine and coworkers<sup>88,89</sup> have found evidence for the dimerization of nitromethane:



The equilibrium constant at  $20^\circ$  is found to be  $\sim 105 \text{ liter mole}^{-1}$  in non-polar solvents. Evidence for dimerization is also indicated

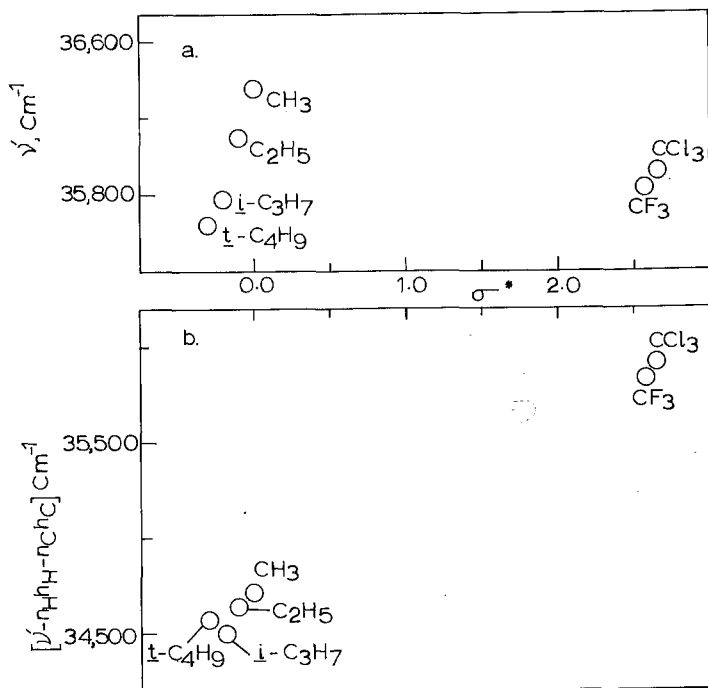


FIGURE 4. Correlation of the  $n \rightarrow \pi^*$  transition frequencies in aliphatic nitro derivatives,  $\text{RNO}_2$  with the polar substituent constants of Taft<sup>87</sup>.

by the infrared data<sup>80</sup>. The absorption spectra of 1,1-dinitroalkanes and trinitromethane in aqueous media have been reported and the color formation in aqueous solution is attributed to the anion<sup>90</sup>.

Nitro olefins show high-intensity bands due to  $\pi \rightarrow \pi^*$  transitions in the region 220–250  $\text{m}\mu$ <sup>91</sup>. The long wavelength  $\pi \rightarrow \pi^*$  transition undoubtedly arises from the conjugation of the nitro group with the  $\text{C}=\text{C}$  bond. In conjugated nitro compounds the  $n \rightarrow \pi^*$  bands are generally masked by the intense  $\pi \rightarrow \pi^*$  absorption bands. Absorption data of a few nitroalkenes have been reported by Montagne and Arnaud<sup>92</sup>.

### B. Aromatic and heterocyclic nitro compounds

The electronic absorption spectra of most of the nitroaromatics reported in the literature refer to the aromatic absorption. The absorption bands due to the nitro group are generally hidden under

the intense bands due to the  $\pi \rightarrow \pi^*$  transitions of the aromatics. The nitro group, being very highly electron-withdrawing in nature, causes marked bathochromic shifts of the aromatic absorption bands and also considerable variation in the intensities. A number of workers have examined the absorption spectra of aromatic nitro compounds and have discussed the effects of substituents, solvents and other environmental factors.

The electronic absorption data of nitrobenzene in different solvents are summarized<sup>93</sup> in Table 7. The band at  $\sim 260 \text{ m}\mu$  found in

TABLE 7. Electronic absorption data of nitrobenzene<sup>93</sup>.

Solvent	$\lambda_{\text{max}} \text{ m}\mu$	$\epsilon_{\text{max}}$
Gas phase	240	7600
Naphtha	251	9200
Cyclohexane (conc. = 2.2-88 mg/liter)	252	9000
Isooctane	252	8620
Ethanol (conc. = 70 mg/liter)	257	8100
Ethanol (conc. = 1.75 mg/liter)	258	7700
95% Aqueous ethanol	260	8000
Dioxane (conc. = 90.5 mg/liter)	257-258	8400
Dioxane (conc. = 1.81 mg/liter)	259	7400
50% Aqueous dioxane	263-265	7800
Water (conc. = 2.4-95 mg/liter)	265-266	7900
1 N NaOH	266	6900
0.1 N HCl	266	7800
Conc. $\text{H}_2\text{SO}_4$	287.5	8600

various solvents is broad and structureless and probably corresponds to the  $203 \text{ m}\mu$  band of benzene<sup>85</sup>. The intensity of the band does not show appreciable concentration-dependence. The band is shifted to higher wavelengths with the increase in dielectric constant of the solvent. The long wavelength absorption band of nitrobenzene (corresponding to the forbidden  $\pi \rightarrow \pi^*$  transition of benzene around  $260 \text{ m}\mu$ <sup>85</sup>) can only be identified with difficulty<sup>93</sup>. This band of nitrobenzene occurs at  $\sim 290 \text{ m}\mu$  ( $\epsilon_{\text{max}} \sim 1500$ )<sup>93</sup>.

Nagakura and coworkers<sup>94</sup> have examined the electronic absorption spectrum of nitrobenzene in the vapor state down to the vacuum ultraviolet region, (see Figure 5 for the spectra of nitrobenzene in vapor and solution phases), and have identified a strong band at  $164 \text{ m}\mu$  and another composite band at  $193 \text{ m}\mu$ . The band around  $240 \text{ m}\mu$  ( $\sim 260 \text{ m}\mu$  in solution phase) has been assigned to intramolecular charge-transfer. This assignment is confirmed by the

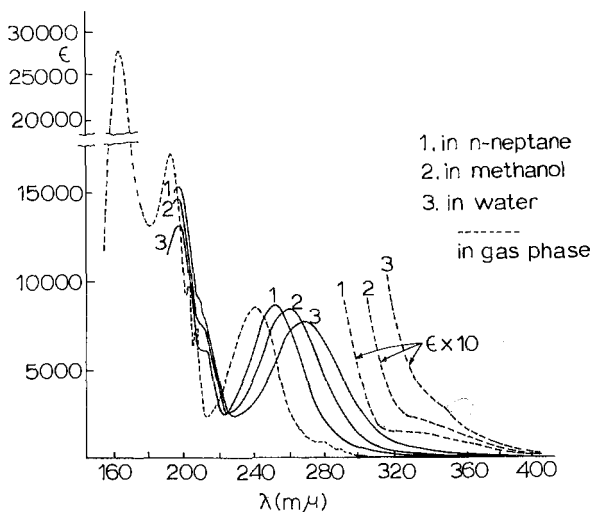
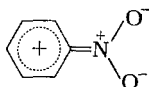


FIGURE 5. The ultraviolet spectra of nitrobenzene in different media<sup>94</sup>.

observation that the intensity is lower in nitromesitylene. Nagakura and coworkers<sup>94</sup> conclude that there is  $\sim 6\%$  contribution of the following charge-transfer structure:



Matsuoka and I'Haya<sup>95</sup> have made detailed calculations on the electronic structure of nitrobenzene employing the Pariser-Parr-Pople-Brown-Heffernon method and found that the calculated energies and intensities agree well with the experimental values. S.C.F. calculations involving configuration interaction have yielded the long wavelength  $\pi \rightarrow \pi^*$  transition energy in fair agreement with the experiment<sup>96</sup>. Electronic structure and spectra of 1,5-dinitronaphthalene<sup>97</sup> and *sym*-trinitrobenzene<sup>98</sup> have also been examined recently.

The effect of *para*-, *meta*-, and *ortho*-substituents on the electronic absorption spectrum of nitrobenzene has been studied exhaustively. Data on a few derivatives are given in Tables 8, 9, and 10. The effect of the substituents in the *para*-, *meta*- and *ortho*-derivatives has been discussed in terms of mesomeric and steric interactions<sup>95,98</sup>. The magnitude of the wavelength shifts by substituents in *para*-substituted nitrobenzenes, is determined by the electrical property

TABLE 8. Absorption maxima of *para*-substituted nitrobenzenes<sup>93</sup>.

Substituent	Solvent	$\lambda_{\max}$ m $\mu$	$\epsilon_{\max}$	$\lambda_{\max}$ m $\mu^a$	$\epsilon_{\max}$
<i>p</i> -Amino-	2 N HCl	258	8,700	—	—
<i>p</i> -Nitro	Methanol	258	14,700		
<i>p</i> -Acetyl-	Cyclohexane	258	14,000	ca 292	2000
				ca 308	1000
	Ethanol	261	14,000	ca 298	2200
				ca 312	1200
<i>p</i> -Carboxy-	Cyclohexane	255	13,000	ca 294	2000
	Ethanol	258	12,000	ca 294	2500
	water	271	10,000		
	0.1 N HCl	263.5	12,500		
	1 N NaOH	272	10,600		
<i>p</i> -Formyl-	Hexane	259	13,800	ca 284	3400
				ca 295	2100
				ca 305	1200
	Const. boiling <i>ethanol</i>	265	11,400		
	Water	266	14,500	ca 301	3000
				ca 314	1800
<i>p</i> -Fluoro-	Isooctane	256	7,600		
	95% Aqueous <i>ethanol</i>	ca 266	7,900		
<i>p</i> -Chloro-	95% Aqueous <i>ethanol</i>	ca 272	10,000		
	pH 6	280	10,300		
<i>p</i> -Bromo-	95% Aqueous <i>ethanol</i>	ca 276	11,100		
<i>p</i> -Iodo-	95% Aqueous <i>ethanol</i>	ca 294	11,700		
<i>p</i> -Methyl-	Isooctane	264	10,250		
	pH 6	285	9,250		
<i>p</i> - <i>i</i> -Propyl-	Isooctane	265	10,430		
<i>p</i> - <i>t</i> -Butyl-	Isooctane	265	10,720		
<i>p</i> -Hydroxy-	Cyclohexane	295	11,000		
	Ethanol	314	13,000		
	Water	314	9,500		
	pH 3	317.5	10,000		
	1 N NaOH	402.5	19,200		
<i>p</i> -Methoxy-	Ethanol	305	13,000		
	Water	313	10,500		
<i>p</i> -Amino-	Naptha	320	14,600		
	Ethanol	371	15,500		
	Water	373-377	13,000		
	0.1 N HCl	372	5,600		
	1 N NaOH	373-379	13,000		
<i>p</i> -Dimethyl- amino-	Ethanol	387	18,300		

<sup>a</sup> Values in italics represent inflexions.

TABLE 9. Absorption maxima of *meta*-substituted nitrobenzenes<sup>93</sup>.

Substituent	Solvent	$\lambda_{\max} \text{ m}\mu^a$	$\epsilon_{\max}$	$\lambda_{\max} \text{ m}\mu^a$	$\epsilon_{\max}$
<i>m</i> -Nitro-	Cyclohexane	228	20,500	ca 275	1150
				283	1000
				294	770
<i>m</i> -Acetyl-	96 % Aqueous <i>ethanol</i>	235	17,400		
	Water	241.5	16,300	305	1100
	Cyclohexane	224	23,000	ca 288	1100
		254	7,000	298	750
		226	22,500	ca 300	800
<i>m</i> -Formyl-	Cyclohexane	ca 260	6,500		
		225	26,000	287	1000
		ca 242	11,000	298	700
		ca 252	6,800		
		ca 256	7,700		
<i>m</i> -Carboxy-	Ethanol				
	Cyclohexane containing 2 % ether	250-251	7,400	ca 285	1150
				ca 296	650
	Ethanol	215	22,500		
		255	7,000		
	Water	212.5	20,000		
		265	7,000		
	0.1 N HCl	261	7,100		
	1 N NaOH	266	7,350		
	Isooctane	246	7,400	284	1700
<i>m</i> -Fluoro-	95 % Aqueous <i>ethanol</i>	ca 255	7,700	ca 300	1900
	95 % Aqueous <i>ethanol</i>	ca 258	7,200	ca 300	1500
<i>m</i> -Chloro-	Water	224	6,800	313	1300
		264	7,100		
		ca 259	6,200	ca 303	1200
<i>m</i> -Bromo-	95 % Aqueous <i>ethanol</i>	ca 259	6,200	ca 308	1000
<i>m</i> -Iodo-	Light petroleum	ca 260	6,200	ca 315	1000
	95 % Aqueous <i>ethanol</i>	ca 262	6,400	ca 292	1500
<i>m</i> -Methyl-	Isooctane	256.5	8,160	ca 292	1500
<i>m</i> - <i>t</i> -Butyl-	Isooctane	258	8,220	ca 292	1500
<i>m</i> -Hydroxy-	Cyclohexane (containing ca. 1 % ether)	225-226	11,000	319	2200
		262	5,750		
	Ethanol	270.5	6,900	332.2	2700
	Water	228	7,600	323	1900
		272	6,000	328	1950
		273.5	6,000	333	1960
	pH 3	228.5	7,900		
		273.5	6,000		
	0.1 N NaOH	251.5	11,000	392	1500
		291	4,500		
	Cyclohexane	223	13,000	313	2400
		260	6,100		
		268	6,400	325.2	2400
	Ethanol	228	8,900	330	2050
		273.5	6,000		
<i>m</i> -Amino-	Ethanol	233	18,000	375	1600
		224	13,500	350-358	1400
		278-279	4,500		
	1 N NaOH	224	14,000	354	1400
		278-279	4,650		
		256	7,500		
	0.1 N HCl	246	23,000	400.3	1350
<i>m</i> -Dimethyl- amino-	Ethanol	246	23,000	400.3	1350

TABLE 10. Absorption maxima of *ortho*-substituted nitrobenzenes<sup>93</sup>.

Substituent	Solvent	$\lambda_{\max} \text{ m}\mu^a$	$\epsilon_{\max}$	$\lambda_{\max} \text{ m}\mu^a$	$\epsilon_{\max}$
<i>o</i> -Acetyl	Cyclohexane	254	6000	—	—
	Ethanol	257	6000		
<i>o</i> -Formyl-	Cyclohexane	222	15300	ca 285	1700
		247	7000		
	Ethanol	220	8500	270	3600
		252	4700		
<i>o</i> -Carboxy-	Cyclohexane (containing ca 2% ether)	—	—	ca 278	1350
	Ethanol	ca 250	3500		
	Water	ca 266	5300		
	0.1 N HCl	ca 262.5	5500		
	1 N NaOH	267	5500		
<i>o</i> -Fluoro-	Isooctane	242	7250	278	1850
	95% Aqueous <i>ethanol</i>	ca 250	6900	ca 285	2200
<i>o</i> -Chloro-	95% Aqueous <i>ethanol</i>	ca 252	3500	ca 290	1200
	Water	228	4400	310	1400
		260	4000		
<i>o</i> -Bromo-	95% Aqueous <i>ethanol</i>	ca 255	3000	ca 292	1300
<i>o</i> -Iodo-	95% Aqueous <i>ethanol</i>	ca 260	3500	ca 310	1500
<i>o</i> -Methyl-	Isooctane	250	5950	ca 290	1500
<i>o</i> - <i>i</i> -Propyl-	Isooctane	247	3760	ca 290	1300
<i>o</i> - <i>t</i> -Butyl-	Isooctane	—	—	ca 275	700
<i>o</i> -Methyl-	Water	266	5300	325	1300
<i>o</i> -Hydroxy-	Cyclohexane	269-270	7500	342	3800
	Ethanol	273	6600	343.5	3600
	Water	ca 230	3700	346	3000
		276	6350		
	pH 3	230	3900	351	3200
		278.5	6600		
	0.1 N NaOH	250	5000	416	4800
		282	4300		
<i>o</i> -Methoxy-	Cyclohexane	249	3400	304	2500
	Ethanol	258.5	3450	317.2	2850
	Water	264	4300	333	2900
<i>o</i> -Amino-	Cyclohexane	227	18000	370	5000
		268	5000		
	Ethanol	275.2	5100	403.6	5400
	Water	233	17000	400-405	4500
		280	5500		
	0.1 N NaOH	245	7000	412	4500
		282.5	5400		
<i>o</i> -Dimethyl- amino-	Ethanol	245.5	21500	416	2950

<sup>a</sup> Values in italics represent inflexions.



of the other substituent. The bathochromic shifts will be large when the other substituents are electron-donating<sup>85</sup>. Thus, *para*-nitroaniline and *para*-dinitrobenzene exhibit the principal absorption bands at 370 and 258  $m\mu$ , respectively, in alcohol solution; nitrobenzene shows this band at 257  $m\mu$ . In *para*-substituted nitrobenzenes the mesomeric interaction is found to be appreciably greater than in *para*-substituted acetophenones<sup>93</sup>.

Rao<sup>99</sup> has found that the position of the principal absorption bands of *para*-complimentary substituted benzene derivatives can be linearly correlated with the Hammett  $\sigma$  constants of the *para*-substituents (Figure 6). In the case of *para*-complimentary substituted

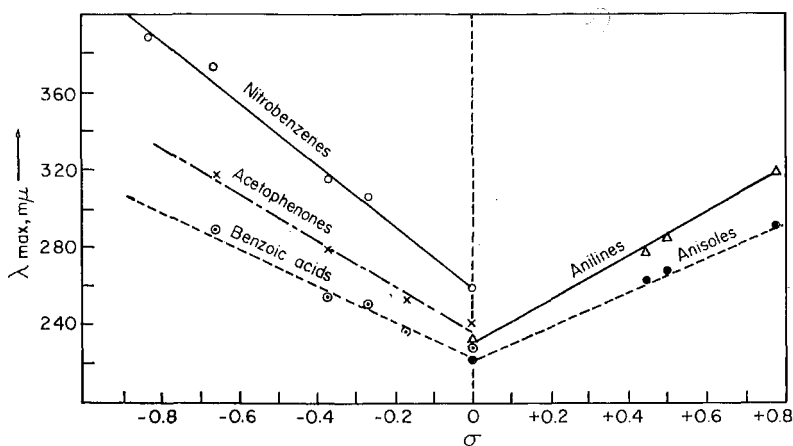


FIGURE 6. Correlation of the absorption maxima of *para*-disubstituted benzenes with Hammett  $\sigma$  constants<sup>99</sup>.

nitrobenzenes<sup>100</sup>, the correlation coefficient is found to be 0.96 and the  $\rho$ -value is  $-159$ . The correlation is not satisfactory with resonance parameters of substituents alone. The correlation of the  $\lambda_{\max}$  values with the substituent constants is not satisfactory if data of the *meta*-substituents are also included. This is understandable since in *meta*-derivatives there will be no mesomeric interaction. The ultraviolet absorption data of *meta*-substituted nitrobenzenes are often quite similar to those of the mono-substituted parent compounds<sup>93</sup>. Some evidence for the buttressing effect in *meta* substituted nitrobenzene derivatives has been found from the electronic absorption spectra<sup>93,101</sup>.

In *ortho*-alkyl substituted nitrobenzenes the intensity of the absorption bands decreases with the increase in the size of the *ortho*-alkyl substituent. Some of the observed effects can be accounted for by the non-planarity of the nitro group which varies with the solvent<sup>93</sup>. Decrease in band intensity and lowering of the  $\lambda_{\max}$  value due to steric effects have been found in *ortho*-alkyl substituted nitrobenzenes<sup>102a</sup> and other related derivatives<sup>102b</sup>. In 2-nitrobiphenyl, a bathochromic shift is found due to increased conjugation<sup>103</sup>.

Recently, the correlations of the electronic ion absorption spectra with the substituent constants and other structural parameters have been reported for a number of nitrobenzene derivatives such as 4-substituted 2-nitroanilines<sup>104</sup>, mono-, di-, and trinitrobenzenes and toluenes<sup>34</sup>, 2,4-dinitrophenylhydrazone derivatives of substituted acetophenones<sup>105</sup>, and various nitrobenzene derivatives<sup>106,107</sup>. The position of the  $n \rightarrow \pi^*$  transition band of the nitro group has been reported in some nitro derivatives by Kiss and Horvath<sup>108</sup>.

The wavelengths corresponding to the absorption maxima of *para*-halogen substituted benzene derivatives are in the order  $I > Br \geq Cl > F$ <sup>85</sup>. This is exactly in the reverse order to the normally expected trend based on the resonance parameters of the halogen substituents. Schubert and coworkers<sup>109</sup> have studied the ultraviolet absorption spectra of *para*-halonitrobenzenes and *para*-haloanisoles, and have interpreted the results in terms of the polarizability of the halogen substituents. Schubert and Robins<sup>110</sup> have also examined the spectra of *para*-alkyl nitrobenzene and found that the neopentyl group is the most effective electron-releasing alkyl group, possibly due to its greater polarizability or to the relief of the strain on excitation (Table 11).

TABLE 11. Principal absorption bands of alkylnitrobenzenes in the near ultraviolet region<sup>110</sup>.

$p\text{-RC}_6\text{H}_4\text{NO}_2$ R	Gas phase $\lambda_{\max}$ , m $\mu$	Heptane $\lambda_{\max}$ , m $\mu$
H	239.1	252.3
CH <sub>3</sub>	250.2	264.1
CH <sub>3</sub> CH <sub>2</sub>	251.0	265.0
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	251.6	265.5
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	252.5	266.3
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	253.2	267.4

A number of papers have appeared in recent years on the ultraviolet absorption spectra of aromatic nitro compounds: nitrohalophenols<sup>111</sup>, vinyl ethers of nitro and halonitrophenols<sup>112</sup>, nitroanthranilic acid and its derivatives<sup>113</sup>, nitrobenzoic acids<sup>114</sup>, ethyl nitrobenzoates<sup>115</sup>, aromatic nitroamino compounds (nitroanilines, di-, and trinitroanilines, etc.)<sup>116-119</sup>, 4-nitroazoxybenzene,<sup>120</sup> 1,2-diphenyl-3-nitrocyclopropene<sup>121</sup>, 4-substituted 2-nitrophenylazides<sup>122</sup>, *N*-( $\alpha$ )-2,4-dinitrophenyl-sulfonylamino acids<sup>123</sup>, 5-nitrofuryl polyenes<sup>124</sup>, substituted nitroformaldehyde phenylhydrazines<sup>125</sup>, and *N*-nitrobenzamides<sup>126,127</sup>.

The ultraviolet absorption data on nitropyridines have been reported<sup>128</sup> as, 2-NO<sub>2</sub>,  $\lambda_{\max}$  292 m $\mu$  ( $\epsilon_{\max}$ , 4000); 3-NO<sub>2</sub>,  $\lambda_{\max}$  242 m $\mu$  ( $\epsilon_{\max}$ , 6000); and 4-NO<sub>2</sub>,  $\lambda_{\max}$  282 m $\mu$  ( $\epsilon_{\max}$ , 2700). The inductive effect of the nitro group lowers the energy of the lowest unoccupied antibonding  $\pi$  orbital to a greater extent in the 4-position than in the other two<sup>128</sup>. The energy of the highest occupied  $\pi$  orbital, on the other hand is lowered to a greater extent in the 2 and 3 positions than in the 4-position. The expected blue shift arising from the nitro group in the 2- or 3-position of pyridine, due to the inductive effect, is not observed except in 3-nitropyridine. This may be because the conjugative effect may predominate over the inductive effect in the other two derivatives<sup>129</sup>. Absorption spectra of nitropyridines and aminonitropyridines have been studied both experimentally and theoretically by Favini and coworkers<sup>130</sup>.

Electronic absorption spectra of nitrofurans<sup>131</sup>, nitration products of chlorofuroxans<sup>132</sup>, nitroisoxazoles<sup>133</sup>, *N*-nitropyrrolidones<sup>134</sup>, mono-nitro derivatives of thiophene analogs of chalcones and dibenzylideneacetone<sup>135</sup>, and *para*-nitrophenetole<sup>136</sup> have been reported in the literature.

### C. Nitro derivatives and analysis

2,4-Dinitrophenylhydrazones are often prepared as derivatives of carbonyl compounds. The electronic absorption spectra of 2,4-dinitrophenylhydrazones are of great use for the qualitative and quantitative analysis of carbonyl compounds<sup>85</sup>. 2,4-Dinitrophenylhydrazones of saturated carbonyl compounds (aldehydes and ketones) absorb at  $\sim 360$  m $\mu$  ( $\epsilon_{\max}$  20,000) while those of  $\alpha,\beta$ -unsaturated derivatives absorb at  $\sim 380$  m $\mu$  ( $\epsilon_{\max}$  25,000). Data on the DNPH derivatives have been given by Gillam and Stern<sup>137</sup> as well as Phillips<sup>138</sup>. There are several papers in the literature dealing with

the analysis of aldehydes and ketones employing the electronic absorption spectra of the DNPH derivatives<sup>139,140</sup>. The molecular weights of aldehydes and ketones can also be determined by employing the ultraviolet absorption of 2,4-dinitrophenylhydrazones<sup>85</sup>.

Alcohols are often determined by making use of the ultraviolet absorption ( $\lambda_{\max} \sim 253 \text{ m}\mu$ ) of alkyl nitrobenzoates<sup>141</sup>. The molecular weights of saturated alcohols can be determined by employing the absorption data of  $\beta$ -2,4-dinitrophenylpropionyl esters<sup>142</sup> ( $\lambda_{\max} 242 \text{ m}\mu$ ,  $\epsilon_{\max} 14,000$ ).

Methods of determination of 5-nitrofurans<sup>143</sup>, nitrofurazone<sup>144</sup>, 5-nitro-2-furaldehyde semicarbazone<sup>145</sup>, nitroarginine in synthetic polypeptides<sup>146</sup> and trypsin and chymotrypsin as *para*-nitroanilide derivatives<sup>147</sup> by utilizing the electronic absorption data have been described in the literature.

#### D. Solvent effects

Balasubramanian and Rao<sup>148</sup> have studied the effects of non-polar, polar, and proton-donating solvents on the  $n \rightarrow \pi^*$  transition of nitromethane exhaustively. The shifts of the absorption maximum in non-polar and polar solvents have been related to the electrostatic interaction between the solute and solvent molecules employing the theory of McRae<sup>149</sup>. In solvents which can donate protons, however, the solvent-shifts are mainly determined by hydrogen bonding between the solvent and the solute molecules. The dipole moment of nitromethane in the electronically excited state has been estimated to be 2.13 debye compared to 3.1 debye in the ground state.

Nitrobenzene shows appreciable solvent red shifts of the principal  $\pi \rightarrow \pi^*$  band in polar solvents:

solvent	water	ethanol	heptane	vapor
$\lambda_{\max}, \text{m}\mu$	265.5	258	252	240

The increased ease of excitation in polar solvents is probably due to the solvation of the excited state; the excited state is likely to have a dipolar quinoid structure<sup>84</sup>.

Abe<sup>150</sup> has studied the effect of solvent on nitro-, dinitro-, and trinitrobenzenes. Solvent effects on the ultraviolet absorption of *para*-substituted nitroanilines have been studied by Utley<sup>151</sup> and Pearson<sup>152</sup>. These authors have discussed the various factors causing the solvent shifts and correlated the solvent shifts with parameters

such as dielectric constants and Z-values. Crandall and Olguin<sup>153</sup> have studied solvent effects on the electronic absorption spectra of a number of substituted nitrobenzenes and correlated the observed red shifts in polar solvents with substituent constants.

### E. Acid-base equilibria

Study of the electronic absorption spectra and acid base equilibria of nitro compounds have yielded very interesting results. The protolytic equilibria of nitroalkanes have been examined<sup>154</sup> and the spectra of the aci-tautomers have been derived. The aci-tautomers show small blue shifts compared to the corresponding anions. The aci forms are stronger acids in the excited state than in the ground state<sup>154</sup>. Absorption spectra of 1,1-dinitroalkanes and trinitromethane determined at different pH values of the media do not show evidence for the aci forms<sup>89</sup>.

Absorption spectra of nitrobenzene, dinitrobenzene, and nitrophenols have been recorded as a function of the pH of the media<sup>155</sup>. Dissociation of trinitromethyl carbinols in aqueous solution has been determined by electronic absorption spectroscopy<sup>156</sup>.

The frequencies of the long wavelength bands of a number of 4-substituted 2-nitrophenols ( $\lambda_{\max} \sim 345 \text{ m}\mu$ ) and of the corresponding phenolate ions ( $\lambda_{\max} \sim 420 \text{ m}\mu$ ) have been correlated with Brown's  $\sigma^+$  constants<sup>157</sup>. Similar studies have also been carried out with 5-substituted 2-nitrophenols, but the  $\Delta\nu$ - $\sigma^+$  correlation is not satisfactory for these derivatives<sup>158</sup>. Absorption spectra of nitronaphthols in basic and acidic media have been studied and the absorption of the anions ( $\lambda_{\max} 440 \text{ m}\mu$ ) and the acid forms characterized<sup>159</sup>. The equilibria involved in the solution of *para*-nitroaniline in aqueous sodium hydroxide have been studied spectrophotometrically and the results correlated with the acidity functions<sup>160</sup>. The spectra of *ortho*- and *para*-nitroanilines, 2,4-, 3,5-, and 2,6-dinitroanilines, as well as *ortho*-, *meta*-, and *para*-nitroacetanilides have been studied in liquid ammonia in the presence of acid (and base); the nature of the equilibria has been established<sup>161</sup>.

The differences between the absorption frequencies,  $\Delta\nu$ , in neutral and alcoholic solutions of the long wavelength absorption bands of a number of 2,4-dinitrophenylhydrazones of aldehydes and ketones have been correlated with the substituent constants<sup>162</sup>. The approximate p*K* values of the carboxyl group in 2,4-dinitrophenylamino acids have been determined by spectrophotometry<sup>163</sup>. Dissociations

of 5-nitro-1,10-phenanthroline<sup>164</sup>, of nitro derivatives of benzanthrones<sup>165</sup>, and of 2-hydroxypyridines<sup>166</sup> have been examined by employing electronic spectroscopy.

### F. Ions

The electronic absorption spectra of the anions of a few primary and secondary nitroalkanes have been investigated<sup>167</sup>. All the anions show a broad intense band ( $\epsilon \geq 9000$ ) with maxima between 223 and 284  $m\mu$ . The variations in the  $\lambda_{\max}$  values have been interpreted in terms of a simple model based on molecular orbital calculations. The ultraviolet absorption spectra of 1,1-dinitroalkane salts have been correlated with electronic and steric effects of substituents<sup>168</sup>. Where the steric effects were constant, the wavelengths could be correlated with Taft's  $\sigma^*$  constants. The spectra of *N*-(2,4-dinitrophenyl)imidazolium salts have been reported ( $\lambda_{\max}$  350–400  $m\mu$ )<sup>169</sup>.

The absorption spectra of the anion radical  $\text{PhNO}_2^-$ , produced by the electrolytic reduction of nitrobenzene shows five peaks in the 390–450  $m\mu$  region<sup>170</sup>. The long wavelength absorption maxima of the radical anions of a few aromatic nitro compounds have been reported by Kemula and Sioda<sup>171</sup> along with the polarographic half-wave potentials. Nagakura and coworkers<sup>172</sup> have found bands at 292 and 560  $m\mu$  for the nitrobenzene anion produced by metal reduction (Figure 7) and bands at 302, 607 and 875  $m\mu$  for the nitrotoluene anion. The spectral results have been discussed on the basis of the electronic structure.

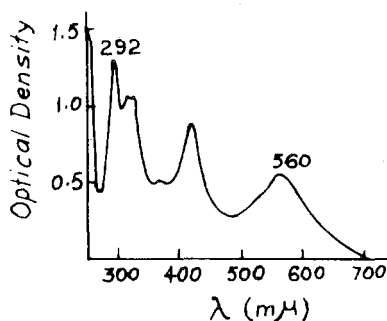


FIGURE 7. Electronic absorption spectrum of nitrobenzene radical anion<sup>172</sup>.

Abe<sup>150,173</sup> has studied the absorption bands of nitro-, dinitro-, and

trinitrobenzene derivatives in alkaline solutions. Trinitrobenzene gives rise to a red color on treatment with sodium hydroxide and the spectrum resembles that of tetryl, thus lending evidence for Meisenheimer's structures. The spectrum of picric acid does not vary with solvent appreciably indicating complete dissociation in all the solvents. The visible spectra of a series of Meisenheimer compounds have been reported<sup>174</sup> and the results are compared with those of mixtures of 1,3,5-trinitrobenzene and sodium methoxide. Electronic absorption spectroscopy has been employed to study the interaction of aromatic nitro compounds (which are electron acceptors) with bases<sup>175</sup>. The studies have been of value in establishing the formation of complexes in these donor-acceptor systems. Visible absorption spectra of 2,4-dinitrophenylhydrazones in alkaline media have been investigated and their utility in quantitative estimations has been pointed out<sup>176</sup>.

The electronic absorption spectrum of the 3-nitropyridine anion radical shows bands at 304 and 460  $m\mu$ ; assignments of these bands have been made<sup>177</sup>.

#### IV. MICROWAVE SPECTRA

The microwave spectrum of nitromethane has been examined by Dailey and Wilson<sup>178</sup>, Bak and coworkers<sup>179</sup>, and Erlandsson<sup>180</sup>, and the data on the relative intensities and Stark effects are available. More recently, the assignments for  $J = 1$  to  $J = 2$  and  $J = 2$  to  $J = 3$  transitions of nitromethane have been assigned by Tannenbaum and coworkers<sup>181</sup> for  $\text{CH}_3\text{NO}_2$  and  $\text{CD}_3\text{NO}_2$ . The best values of rotational constants of B and C are found to be 10,542.7 and 5876.6 Mc/sec for  $\text{CH}_3\text{NO}_2$  and 8697.1 and 5254.3 Mc/sec for  $\text{CD}_3\text{NO}_2$ . The rotational constant for the  $\text{NO}_2$  group about the symmetry axis is 13,277.5 Mc/sec, while the barrier to internal rotation ( $V_6$ ) is 6.03 cal/mole for  $\text{CH}_3\text{NO}_2$  and 5.19 cal/mole for  $\text{CD}_3\text{NO}_2$ . The microwave spectrum of methyl nitrate has also been studied recently<sup>182</sup>.

The microwave spectrum of nitrobenzene has been studied<sup>183</sup> and the moments of inertia are found to be  $I_a^0 = 126.0$ ;  $I_b^0 = 393.7$  and  $I_c^0 = 518.8$  amu  $\text{\AA}^2$ , and the molecule is planar as expected.

#### V. NUCLEAR MAGNETIC RESONANCE SPECTRA

Chemical shifts of protons in nitroalkanes have been explained in terms of the inductive effect of the  $\text{NO}_2$  group and the effect of diamagnetic anisotropy of the C—C bonds<sup>184</sup>. The inductive effect

of the  $\text{NO}_2$  group operates as far as the fourth carbon atom in the chain. The ranges of chemical shifts for various types of protons in nitroalkanes are quite narrow (Table 12). The nuclear magnetic resonance spectra of 3-nitropropene and 1-nitropropene and the analysis of their mixtures have been reported<sup>185</sup>. A good correlation has been found between the electronegativity of the substituents and the three proton coupling constants of the vinyl group in compounds of the type  $\text{CH}_2=\text{CHX}$ ; when  $\text{X} = \text{NO}_2$ , the coupling constants<sup>186</sup> were:  $J_{\text{gem}}$ ,  $-2.0$ ;  $J_{\text{cis}}$ ,  $7.6$ ; and  $J_{\text{trans}}$ ,  $15.0$  c.p.s.

TABLE 12. Proton chemical shifts in nitroalkanes.

	$\tau^a$		$\tau^a$
$\text{CH}_3\text{NO}_2$	5.72	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{NO}_2$	5.70
$\text{CH}_3\text{CH}_2\text{NO}_2$	5.62	$\text{CH}_2(\text{NO}_2)_2$	3.90
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	5.70	$\text{CH}_3\text{CH}(\text{NO}_2)_2$	3.72
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{NO}_2$	5.67	$\text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)_2$	3.83
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{NO}_2$	5.70	$\text{CH}(\text{NO}_2)_3$	2.48

<sup>a</sup> TMS reference;  $\tau$  of protons on the carbon adjacent to  $\text{NO}_2$

The nmr spectra of aci-nitroanions have been examined<sup>187</sup> and the equilibrium,  $\text{RCH}_2\text{NO}_2 + \text{B}^- \rightleftharpoons \text{RCHNO}_2^- + \text{HB}$ , has been shown to lie far to the right; NMR spectroscopy is thus found to be useful in the study of nitro compounds and their anions. The nmr spectra of  $\alpha$ -nitrocycloalkanones as well as their salts have been studied<sup>188</sup>. These results along with the infrared and the ultra-violet data have been of value in the study of enolization of  $\alpha$ -nitroketones.

Conformational preference of the  $\text{NO}_2$  group in nitrocyclohexane has been studied by recording the nmr spectra in different media and the conformational free energy difference has been estimated to be  $\sim 0.8$  Kcal/mole<sup>189</sup>. The (equatorial/axial) equilibrium constant for 4-*t*-butyl-1-nitrocyclohexane was found to be  $\sim 5.7 \pm 1.5$  by measurement of the line widths of the signals due to the methine proton (on the carbon atom holding the  $\text{NO}_2$  group)<sup>190</sup>. The conformational equilibria of nitrocyclohexane (**1**) and *cis*-4-methylnitrocyclohexane (**2**) have been investigated by nmr spectroscopy by Franklin and Feltkamp<sup>191</sup> who have calculated the conformational free energy of the nitro group to be 1.3 Kcal/mole in the latter compound. Some of the data given by these workers on **1**, **2** as well as *cis*- and *trans*-4-*t*-butylnitrocyclohexanes (**3** and **4**) are given in Table 13.



TABLE 13. Proton chemical shifts in nitrocyclohexane derivatives<sup>191</sup>.

Compound	Mc/s	Solvent	$\alpha$ -Proton chemical shift	Band width (in c/s)	Coupling constants (in c/s)	
			$\tau$		$J_{aa}$ ,	$J_{ae}$
1	60	CDCl <sub>3</sub>	5.59	27.2		
1	100	CDCl <sub>3</sub>	5.62	29.0	10.35	4.20
3	60	CDCl <sub>3</sub>	5.47	13.0		
3	100	CDCl <sub>3</sub>	5.30	13.0		
3	100	CS <sub>2</sub>	5.63	12.5		
4	60	CDCl <sub>3</sub>	5.69	31.0	11.5	4.0
4	100	CDCl <sub>3</sub>	5.69	31.1	11.55	4.03
4	100	CS <sub>2</sub>	5.86	31.0	11.5	4.0
2	60	CDCl <sub>3</sub>	5.53	19.0		
2	100	CDCl <sub>3</sub>	5.53	19.2		
2 (25°)	100	CS <sub>2</sub>	5.70	19.0		
2 (-80°)	100	CS <sub>2</sub>	5.63	13.0		
			5.82	—		

In 2-nitro-1,3-cyclohexanediol, the NO<sub>2</sub> group has been shown to be in the equatorial position and *trans* to both the OH groups by a study of the nmr spectrum of the acetate<sup>192</sup>.

The stereoisomers about the C=N bond in 2,4-dinitrophenylhydrazones and semicarbazones of ketones have been examined by nmr spectra<sup>193</sup>. The  $\alpha$ -hydrogens *syn* to the anisotropic group are shielded while the  $\beta$  and  $\gamma$ -hydrogens *syn* to the anisotropic group are deshielded. The magnitude of the chemical shifts between the *syn* and the *anti* protons is nearly independent of the solvents. The proportions of *syn* and *anti* isomers have been determined by integrating the areas under the appropriate nmr signals. The tetra-*o*-acetyl derivative of dinitroinositol shows an equal intensity doublet due to the protons of the acetoxy group and four equal intensity doublets displaying large splitting due to axial-axial spin coupling. The signal of the two equivalent protons of the molecule is split by the spin-spin interaction with the two adjacent axial protons giving rise to 1:2:1 triplet for the equatorial protons<sup>194</sup>.

The nmr spectrum of nitroethylene has been reported and the protons *cis* to the nitro group appear at lower field (0.68 ppm) than the protons *trans* to the nitro group<sup>195</sup>. The nmr results of substituted benzenes correlate with the expected  $\pi$  electron densities in the *para* position<sup>196</sup>. For nitrobenzene the shielding parameters are: *o*, -0.93; *m*, -0.21; and *p*, -0.33 ppm. The coupling constants and

chemical shifts at infinite dilution in cyclohexane for *para*-substituted nitrobenzenes ( $A_2B_2$  system)<sup>197</sup> are summarized in Table 14. The ring proton chemical shifts in polysubstituted benzenes have been reported with an accuracy of 0.1 ppm, as simple sums of substituent shielding constants, except in the case of *ortho* substituents; the nmr data of the nitro derivatives also fit into this correlation<sup>198</sup>. The  $^{13}\text{C}$  coupling constants in some nitrobenzene derivatives have been measured<sup>199</sup>: 2,4,6-trinitrophenol (acetone),  $J_{13\text{OH}} = 175.8 \pm 0.5$ ; 2,6-dinitro-4-chlorophenol (ether),  $J_{13\text{OH}}, 174.1 \pm 0.4$ ; 2,6-dibromo-4

TABLE 14. Coupling constants and chemical shifts in the proton resonance spectrum of substituted nitrobenzenes.<sup>197</sup>

<i>p</i> -Substituents	Shifts <sup>a</sup> (ppm)		<i>J</i>	<i>j</i>	Coupling cps	
					<i>J</i> <sub>A</sub>	<i>J</i> <sub>B</sub>
NH <sub>2</sub> , NO <sub>2</sub>	0.677	−0.627	+9.0	+0.3	+2.6	+2.3
OMe, NO <sub>2</sub>	0.380	−0.887	+9.0	+0.3	+2.7	+2.7
Cl, NO <sub>2</sub>	−0.160	−0.870	+8.7	+0.3	+2.8	+2.2
Br, NO <sub>2</sub>	−0.330	−0.783	+8.9	+0.4	+2.6	+2.2
NO <sub>2</sub> , NO <sub>2</sub>	−1.147					
CH <sub>3</sub> , NO <sub>2</sub>	0.035	−0.825	+8.5	+0.4	+2.3	+2.1

<sup>a</sup> benzene reference

nitrophenol (acetone),  $J_{13\text{HC}}, 172.2 \pm 0.4$ , and 1,3,5-trinitrobenzene (acetone),  $J_{13\text{OH}}, 179.5 \pm 1.5$  c.p.s. The nmr spectrum of 1-fluoro-2,4-dinitrobenzene has been analyzed in detail<sup>200</sup>.

The proton magnetic resonance spectra of several methyl-nitronaphthalenes, *p*-nitrotoluene, and nitro-*p*-xylene have been determined<sup>201</sup>; the NO<sub>2</sub> group has little effect on the chemical shift of the CH<sub>3</sub> group. The anisotropy of the  $\alpha$ -nitro group has been found to have a dominant effect on H<sub>8</sub> shifts of the naphthalene and is expected to be responsible for about half the adjacent proton shifts. The nmr spectra of dinitronaphthalenes have been examined<sup>202</sup> and the effect of the NO<sub>2</sub> group on the ring proton shifts discussed. The nmr spectra of isomeric nitrotoluidines and *para*-nitroaniline have been determined<sup>203</sup>. The conformation of *N*-methyl-2,4,6-trinitroaniline (**5**) and *N*-methyl-2,6-dinitroaniline as well as their analogous *N*-diphenylamino compounds have been studied by recording the nmr spectra at various temperatures<sup>204</sup>. The 3- and 5-phenyl protons are nonequivalent at low temperature, but become equivalent at sufficiently high temperatures. The coalescence of the

AB quartet of the picryl protons with temperature in **5** and 2,2-diphenyl-1-picrylhydrazone has been observed. The life times of the ground state configurations, and the activation energy have been determined. The chemical shifts of the formyl protons of nitrobenzaldehyde<sup>205</sup> and alkoxy groups in some nitro substituted aromatics<sup>206</sup> have been reported.

The <sup>14</sup>N chemical shifts in the nmr spectra of nitro compounds have been measured<sup>207</sup>; the signals were sharp in the case of aliphatic derivatives and show dependence on the electronegativity of the substituent. Some data are given in Table 15. The <sup>14</sup>N chemical

TABLE 15. <sup>14</sup>N Chemical shifts in aliphatic nitro compounds.

Compound	Chemical shift (ref. CH <sub>3</sub> NO <sub>2</sub> ) <sup>a</sup>		
	cps ± 2	p.p.m. ± 0.5	Half width c.p.s. ± 2
CH <sub>3</sub> NO <sub>2</sub>	0	0	24
CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	-49	-12	30
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NO <sub>2</sub>	-41	-10	35
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NO <sub>2</sub>	-41	-10	49
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> NO <sub>2</sub>	-40	-10	56
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> NO <sub>2</sub>	-42	-10	57
(CH <sub>3</sub> ) <sub>2</sub> CHNO <sub>2</sub>	-96	-24	38
Nitrocyclohexane	-80	-20	92
(CH <sub>3</sub> ) <sub>2</sub> (Cl)CNO <sub>2</sub>	-53	-13	35
(CH <sub>3</sub> ) <sub>3</sub> CNO <sub>2</sub>	-125	-30	43
CH(NO <sub>2</sub> ) <sub>3</sub>	+152	+35.5	11
C(NO <sub>2</sub> ) <sub>4</sub>	+206	+48	10

<sup>a</sup> 4.3 Mc/sec at 26°.

shifts were concentration dependent. Increase in the positive inductive (+I) effect shifts the NO<sub>2</sub> signal to lower fields. It is possible to distinguish among primary, secondary, and tertiary nitroalkanes on the basis of <sup>14</sup>N shifts<sup>207</sup>. The <sup>14</sup>N shifts of a number of organic nitro compounds have been determined in dilute solutions in low viscosity solvents<sup>208</sup>.

The <sup>15</sup>N chemical shifts of a number of nitro compounds have been recently reported<sup>209,210</sup>. In nitrobenzene, the diamagnetic contribution is 490 p.p.m. and the chemical shift is 372 p.p.m. (downfield from external anhydrous ammonia, operated at 6.08 Mc. p.s. and 14,100 gauss). In *p*-nitroaniline, the <sup>15</sup>N shift appears to have an

extra paramagnetic contribution, since it does not fit the correlation with  $^{13}\text{C}$  and  $^{19}\text{F}$  chemical shifts<sup>210</sup>. The  $^{15}\text{N}$  chemical shifts of a few *para*-substituted nitrobenzenes relative to nitrobenzene are listed in Table 16.

TABLE 16.  $^{15}\text{N}$  Chemical shifts in *para*-substituted nitrobenzenes.

Substituent	Chemical shifts <sup>a</sup> p.p.m.
$\text{NH}_2$	4.38
OMe	4.38
F	3.57
$\text{NHCOCH}_3$	3.07
Cl	2.09
Br	1.32
H	0.00
CN	-2.58
$\text{NO}_2$	-3.85

<sup>a</sup> In 15 mole % solution in DMSO. A positive shift indicates a shift upfield from nitrobenzene.

Solvent effects on the proton resonance spectra of nitrobenzene, nitromethane, and substituted nitrobenzenes have been reported in the literature<sup>211-213</sup>.

## VI. LITERATURE ON THE SPECTROSCOPIC DATA OF SOME ASSORTED NITRO COMPOUNDS

There are innumerable reports in the recent literature on nitro compounds where the spectroscopic data on infrared, electronic and nmr spectra or of any two of these have been recorded and it is by no means possible to list all of the references in this section. Only a few are listed here: nitrodienes and nitroenynes<sup>214</sup>, spiro Meisenheimer compounds related to 2,4,6-trinitrobenzene<sup>215</sup>, the reaction products of isophyllocladene with diazotized 2,4-dinitroaniline<sup>216</sup>, nitropyridinium salts<sup>217,218</sup>, nitrosteroids<sup>219-222</sup>, nitrocamphor anhydride<sup>223</sup>, 4-nitrobenzyl cyanide in alkaline media<sup>224</sup>, *N*-nitroamides and carbamates<sup>50</sup>, nitrotryptophans<sup>225</sup>, *N*-nitrobenzamides<sup>226</sup>, dinitroacetonitrile and its salts<sup>227</sup>, and Michael reaction products of nitroparaffins<sup>228</sup>.

## VII. SPECTROSCOPIC STUDIES OF HYDROGEN BONDING AND KETO-ENOL EQUILIBRIA

There has been considerable evidence based on spectroscopic investigations that the nitro group can act as a proton acceptor in hydrogen bonding. Recently, Schleyer and coworkers<sup>229</sup> have reviewed the literature up to 1964 on hydrogen bonding of the nitro group. The hydrogen bond interaction of the nitro group is generally weak except in the case of *o*-nitrophenol and its analogs. The intramolecular hydrogen bonding in *o*-nitrophenol is a special case where the high strength of the hydrogen bond results from resonance stabilization. The  $\Delta\nu_{\text{OH}}$  in the infrared spectrum of *o*-nitrophenol is  $\sim 400 \text{ cm}^{-1}$  in contrast to the  $\Delta\nu_{\text{OH}}$  of  $\sim 80 \text{ cm}^{-1}$  found for the interaction of nitrobenzene with phenol.

Infrared studies of Ungnade and coworkers<sup>230, 231</sup> on  $\beta$ -nitroalcohols and diols in solutions showed that they exist mainly in the monomeric state; the observations of these workers will now be summarized.  $\beta$ -Nitroalcohols are nearly monomeric in chloroform solution. They are partially associated in carbon tetrachloride. The association constants in carbon tetrachloride increase with the number of nitro groups. Apparently the tendency for hydrogen bonding in these compounds is related to the electron deficiency on the carbon holding the hydroxyl group. The spectra show free hydroxy and sharp nitro stretching bands indicating the presence of non-bonded species. Some hydrogen bonding with solvent chloroform seems to occur. In the solid state, however, there is appreciable intermolecular hydrogen bonding. The diols show slight lowering of the hydroxyl frequency probably due to association. The positions of  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  bands in  $\beta$ -nitroalcohols and diols are mainly determined by the degree of substitution on the carbon holding the nitro group. Nitromethane inhibits hydrogen bonding in alcohols. The abnormal ultraviolet absorption spectra of  $\beta$ -nitroalcohols may be discussed in terms of specific interaction between solute and solvent molecules.

Schleyer and coworkers<sup>229</sup> have criticized the conclusions of Ungnade and coworkers<sup>230, 231</sup> and have found that the failure to observe bonded OH peaks in  $\beta$ -nitroalcohols by these workers was due to the poor resolution of the instrument employed (NaCl prism). The effect of addition of  $\text{CH}_3\text{NO}_2$  on the spectra is mainly because of the formation of new hydrogen bonds between nitromethane and the alcohols. The  $\Delta\nu_{\text{OH}}$  values depend markedly on the concentration of the proton acceptor (nitro compound)<sup>229</sup>.

Based on the ultraviolet absorption spectra of *m*- and *p*-nitrophenols, as well as nitroanilines in the vapor state and in several solvents, existence of intermolecular hydrogen bonding has been proposed<sup>232</sup>. The ultraviolet spectra of 4-nitro-4'-aminodiphenylmethane and its methyl derivative show that two forms of association can occur in solution namely layer type association and head to tail linear association<sup>233</sup>.

The infrared absorption spectra of the  $\alpha$ - and  $\beta$ -modifications of *p*-nitrophenol have been examined<sup>234</sup>. Stanevich<sup>235</sup> has examined the far infrared absorption spectra (in the 20–240  $\text{cm}^{-1}$  region) of phenol, *ortho*-, *meta*-, and *para*-nitrophenols, 2,6-dinitrophenol, and 2,4-dinitrophenol in the crystalline and liquid states. In phenol and *meta*-, and *para*-nitrophenols, the  $\text{O} \cdots \text{O}$  bond stretching vibration frequency in the solid state has been found at  $\sim 175$ ,  $\sim 125$  and  $\sim 99 \text{ cm}^{-1}$  respectively. The intermolecular hydrogen bond stretching vibration frequency of phenol comes down to  $137 \text{ cm}^{-1}$  in solution phase.

By examining the effects of various hydroxylic solvents on the band due to the  $n \rightarrow \pi^*$  transition of nitromethane, Balasubramanian and Rao<sup>148</sup> have related the solvent blue-shifts to the energies of the hydrogen bond formed between the nitro and the hydroxyl groups. In a series of nitroalkanes ( $\text{RNO}_2$ ) studied, the solvent blue-shifts in a given hydroxylic solvent varies in the order  $\text{Me} > \text{Et} > i\text{-Pr} > t\text{-Bu}$ . For any given nitroalkane, the blue shift in alcohol ( $\text{ROH}$ ) solvents varies in the order,  $\text{CF}_3\text{CH}_2 > \text{Me} > \text{Et} > i\text{-Pr} > t\text{-Bu}$ . Based on these studies, it can be concluded that the nitro group forms hydrogen bonds with alcohols, although the strength is appreciably weaker than in the corresponding carbonyl compounds. The hydrogen bond energies of nitro compounds with alcohols are likely to be of the order of 1.5 Kcal/mole.

By making use of the  $\Delta\nu_{\text{OH}}$  of nitromethane in phenol ( $\text{CCl}_4$  solution) and the relation between  $\Delta\nu_{\text{OH}}$  and  $\Delta H^\circ$  of Singh, Murthy, and Rao<sup>236</sup>, the  $\Delta H^\circ$  has been estimated to be  $\sim 2.5 \text{ Kcal/mole}$ . Recently, Ungnade and coworkers<sup>237</sup> have investigated hydrogen bonding between the nitro group and the alcoholic hydroxylic group employing infrared and nuclear magnetic resonance spectroscopy and have concluded that a weak hydrogen bond is formed in these systems.  $\beta$ -Nitroalcohols and their derivatives have been found to form hydrogen bonds with dioxane, from a study of the nitro group frequencies in the infrared spectra<sup>81</sup>. Evidence has been presented for the association of *p*-nitrophenol by the study of the electronic

spectra in cyclohexane and ether solvents<sup>238</sup>. Ether breaks the intermolecular hydrogen bonds caused by the self-association of nitrophenol and forms new hydrogen bonds by acting as a donor. The effect of addition of ether is seen in terms of a bathochromic shift of the  $280\text{ m}\mu$  band of *p*-nitrophenol; *p*-nitroanisole, as expected, does not show any appreciable difference in the spectra in ether and cyclohexane.

The equilibrium constants and frequency shifts,  $\Delta\nu_{\text{OH}}$ , for the hydrogen bond interaction of nitromethane with a number of hindered alcohols and phenols have been reported by Singh and Rao<sup>239</sup>. The equilibrium constants vary between 0.1 and 2.0 liter/mole while the  $\Delta\nu_{\text{OH}}$  varies between 7 and 70  $\text{cm}^{-1}$ . Hydrogen bonding between *m*-, and *p*-nitroanilines and acetone has been examined by infrared spectroscopy<sup>240</sup>.

The infrared spectra of nitroalcohols have indicated that the structure of these compounds are best represented in terms of intramolecular hydrogen bonds between the hydroxyl and the nitro groups<sup>241</sup>. Kuhn and coworkers<sup>242</sup> have found the bonded hydroxyl band of  $\beta$ -nitroethanol at  $3608\text{ cm}^{-1}$  as compared to the free hydroxyl band at  $3623\text{ cm}^{-1}$ ; they have proposed the *gauche* form for the compound which is stabilized by a weak intramolecular hydrogen bond. Urbański<sup>243</sup> has examined the ultraviolet spectra of a number of nitroparaffin derivatives containing a hydroxyl and/or an amino group, but failed to find the  $270\text{ m}\mu$  ( $n \rightarrow \pi^*$ ) band of the nitro group. This observation has been explained in terms of intramolecular hydrogen bonds between the nitro and the hydroxyl or the amino groups. Ungnade and coworkers<sup>230, 231</sup> questioned the presence of intramolecular hydrogen bonds in  $\beta$ -nitroalcohols, but the recent study of Schleyer and coworkers<sup>229</sup> has clearly confirmed the existence of intramolecular hydrogen bonds in  $\beta$ -nitroalcohols as well as in diols.

As pointed out earlier, the presence of a strong intramolecular hydrogen bond in *o*-nitrophenol is well known. The hydroxyl stretching band in this compound is shifted to much lower frequencies ( $\Delta\nu_{\text{OH}} \sim 400\text{ cm}^{-1}$ ) due to the high strength associated with the resonance-stabilized hydrogen bond. Intramolecular hydrogen bonds in *o*-nitrophenol and related derivatives have been examined by Dabrowska and Urbański<sup>244</sup> by employing infrared spectroscopy. The infrared OH frequencies and nmr chemical shifts of the OH protons of nitrophenols have been correlated<sup>245</sup>. The dependence of the chemical shift on the concentration of the compounds in

solution has also been studied. The stability of the hydrogen bonds in *o*-nitrophenols in different solvents has been examined by infrared and electronic spectroscopy<sup>246</sup>.

The intramolecular hydrogen bonding in *o*-nitroanilines has been examined by Dyall and Hambly<sup>247</sup>, and Urbański and Dabrowska<sup>248</sup>. Moritz<sup>249</sup> has discussed the assignments of the NH stretching band in the overtone region of *o*-nitroaniline. In *o*-nitroaniline, the major effect due to the intramolecular hydrogen bonding is found in the shift of the *sym*-NH<sub>2</sub> stretching vibration to a lower frequency<sup>247, 248, 250</sup> and of the asymmetric stretching band to a slightly higher frequency<sup>250</sup>. The effect of solvents on the NH<sub>2</sub> stretching band of *o*-nitroaniline has been examined and the shift of the NH<sub>2</sub> symmetric band to lower frequencies is found to vary in the order, pyridine > dioxane > acetone<sup>251</sup>. The equilibrium between intramolecularly hydrogen bonded and solvent bonded species in *o*-nitroaniline has been studied by infrared spectroscopy in pyridine solutions<sup>252</sup>. In *o*-nitroaniline only one amino hydrogen is bonded to pyridine. In *o*-nitro-*N*-methylaniline both intramolecular hydrogen bonded species and pyridine bonded species were present<sup>251</sup>. In 2-nitrophenol and 2,6-dinitrophenol, the O · · · O stretching vibration frequencies have been found around 100 cm<sup>-1</sup><sup>235</sup>.

By the measurement of the frequencies and intensities of the fundamental hydroxyl stretching bands and of its first and second overtones of *o*-nitrophenol, it has been shown that the strong hydrogen bonding causes increased mechanical anharmonicity<sup>253</sup>. The mechanical anharmonicity seems to be less in weaker hydrogen bonds. The hydrogen bond interaction in *o*-nitrophenol and *o*-nitroaniline have been treated theoretically by Zubkova and co-workers<sup>254</sup> by the calculation of the electronic energy levels and spectra.

A study of the infrared and ultraviolet spectra of a number of 2,4-dinitrodiphenylamines in different solvents has shown that these compounds are non-planar in many solvents and has also indicated the presence of an intramolecular hydrogen bond<sup>255</sup>. The hydrogen bond is rendered strong in these compounds by the presence of the *para*-nitro substituent which increases the positive charge on the amino group. Pinchas<sup>256</sup> and Forbes<sup>257</sup> have studied the infrared, ultraviolet and nuclear magnetic resonance spectra of *o*-nitrobenzaldehyde and related compounds and have concluded that the aldehydic C—H forms an intramolecular hydrogen bond with the oxygen of the nitro group. The hydrogen bond strength is estimated to be about 2 Kcal/mole.



Intramolecular hydrogen bonding in 2,6-dichloro-*p*-nitrophenol has been examined by microwave absorption studies<sup>258</sup>. The stereospecific nature of the long range spin coupling between aldehydic protons and ring protons has been used to determine the direction of the intramolecular hydrogen bond in 3-nitro- and 5-nitrosalicylaldehyde<sup>259</sup>. Fairly strong intramolecular hydrogen bonding has been shown to be present in *o*-nitroamides by a study of the infrared and electronic spectra<sup>260, 261</sup>. Hydrogen bonding of aromatic nitroamides has been examined by electronic spectra in several solvents. Raman and dipole moment studies of nitroaminobutadiene derivatives have shown that these molecules exist in cyclic hydrogen bonded structures<sup>262</sup>.

Infrared, nuclear magnetic resonance and electronic spectral studies by Feuer and Pivawer<sup>188</sup> of 6-, 8-, and 10-membered  $\alpha$ -nitrocyclanones have shown a high degree of enolization. All these compounds show additional bands in the double bond region (1613 and 1515  $\text{cm}^{-1}$ ) due to the C=C and conjugated nitro group stretching vibrations.

The infrared spectrum of 3-nitro-4-hydroxypyridine shows evidence for the presence of the pyridone form in high proportion<sup>263</sup>. Although the spectral data do not indicate any abnormal structure of 4-nitro-2,6-di-*t*-butylphenol a suggestion has been made that there may be facile tautomerism between the phenol and the quinoid forms<sup>264</sup>.

## VIII SPECTRA OF CHARGE-TRANSFER COMPLEXES

The study of the interaction of various types of electron donors with acceptors has been a subject of intense investigation in recent years<sup>265-268</sup>. Charge-transfer interaction between donors and acceptors generally give rise to new bands in the electronic spectra and the charge-transfer energy ( $h\nu_{\text{c.t.}}$ ) is related to the ionization potential of the donor and electron affinity of the acceptor. Many polynitro compounds are good electron acceptors. A large number of publications have described the electronic and infrared spectra of charge-transfer complexes with polynitro compounds as electron acceptors. The subject has been reviewed recently by Mulliken<sup>265, 266</sup>, Briegleb<sup>267</sup>, and Andrews and Keefer<sup>268</sup>. In this section, the important highlights of the spectra of charge-transfer complexes of nitro compounds will be briefly reviewed.

The charge-transfer absorption data along with the equilibrium constants for the interaction of a few benzene derivatives with

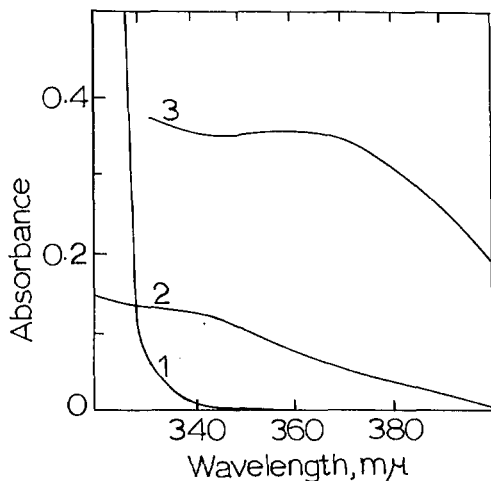


FIGURE 8. Charge-transfer spectrum of naphthalene with *sym*-trinitrobenzene<sup>272</sup>: (1) naphthalene (2) *sym*-trinitrobenzene (3) c.t. complex in  $\text{CCl}_4$ .

*sym*-trinitrobenzene (TNB) (see Figure 8 for a typical charge transfer spectrum) are given in Table 17. Briegleb and Czekalla<sup>269</sup> have reported that the  $h\nu_{\text{c.t.}}$  of these complexes vary linearly with donor ionization potentials (Figure 9) and have shown that the data can be correlated with the relation,

$$h\nu_{\text{c.t.}} = I - C_1 + (C_2/I - C_1)$$

TABLE 17. Charge transfer interaction between *sym*-trinitrobenzene and aromatics<sup>267,268</sup>.

Acceptors	$K^{\text{ca}}$ l. mole <sup>-1</sup>	$\lambda_{\text{max}}$ mμ	$\epsilon_{\text{DA}}$ mole <sup>-1</sup> cm <sup>-1</sup> l.	$-\Delta H$ Kcal mole <sup>-1</sup>
Benzene	0.82	284	9755	1.71
Toluene	1.82	306	4350	1.76
<i>o</i> -Xylene	2.08	312	4080	2.16
<i>m</i> -Xylene				
<i>p</i> -Xylene				
Mesitylene	2.67	335	3270	—
Hexamethylbenzene	5.7 <sup>b</sup>	395	2150	4.71
Naphthalene	17.0	365	1365	4.31
Anthracene	39.8	460	1333	—

<sup>a</sup> Solvent chloroform, temp. 25°; <sup>b</sup> solvent,  $\text{CCl}_4$ .

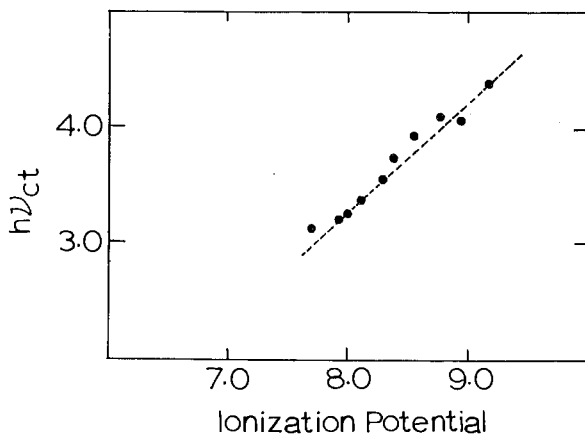


FIGURE 9. Correlation of the charge-transfer transition energy of TNB aromatic complexes with ionization potentials of the donors.

where  $C_1$  and  $C_2$  are 5.0 and 0.70 eV respectively. By simple molecular orbital calculations, it has been found that the charge-transfer transition energy of complexes of aromatics with TNB and 2,4,7-trinitrofluorenone show linear relations with energies of the highest filled donor orbitals<sup>270</sup>. A linear dependence of absorption intensity on the  $\lambda_{c.t.}$  of TNB complexes has also been reported. From a knowledge of the enthalpy of formation and the  $h\nu_{c.t.}$ , the coefficients of the no-bond and dative wave functions in the ground state can be calculated in such weak complexes<sup>267</sup>.

Solvent effects on the equilibrium constant and charge-transfer absorption of the TNB complexes with *N,N*-dimethylaniline<sup>271</sup> and naphthalene<sup>272</sup> have been examined and some typical data are given in Table 18 for the TNB complexes of dimethylaniline.

TABLE 18. Solvent effects on the charge transfer interaction between *sym*-trinitrobenzene and *N,N*-dimethylaniline<sup>271</sup>.

Solvent	Solvent dielectric constant, 20°	$K_c$ l.mole <sup>-1</sup>	$\lambda_{max}$ , m $\mu$	$\epsilon_{max}$ , l.mole <sup>-1</sup> cm <sup>-1</sup>
Cyclohexane	2.07	9.5	470	1300
<i>n</i> -Hexane	1.9	8.2	465	1120
<i>n</i> -Heptane	—	8.2	466	1180
Decalin	—	7.2	472	1300
Carbon tetrachloride	2.25	3.4	484	1340
Chloroform	4.5	1.3	486	1140
<i>s</i> -Tetrachloroethane	—	0.2	492	—
1,4-Dioxane	2.1	0.15	465	—

Data on the complexes of a few substituted benzene derivatives with tetranitromethane are given in Table 19.

The acceptor strength of *sym*-TNB compared to the other acceptors is given by the order, Tetracyanoethylene > ICl > TNB > Picric acid > I<sub>2</sub> > *p*-Benzoquinone. Polynitro acceptors form increasingly stable complexes with *n*-alkylanilines as the number of nitro groups is increased<sup>274</sup>: nitrobenzene < *ortho*- and *meta*-dinitrobenzenes < *para*-dinitrobenzene < 1,3,5-trinitrobenzene. In

TABLE 19. Equilibria between tetranitromethane and substituted benzenes<sup>273</sup>.

Benzene substituents	K at 20.8° <sup>a</sup>
H	0.007
CH <sub>3</sub>	0.14
<i>o</i> -(CH <sub>3</sub> ) <sub>2</sub> } <i>m</i> -(CH <sub>3</sub> ) <sub>2</sub> } <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> }	1.00
1,3,5-(CH <sub>3</sub> ) <sub>3</sub>	3.27
1,2,4,5-(CH <sub>3</sub> ) <sub>4</sub>	4.10
(CH <sub>3</sub> ) <sub>5</sub>	5.60
(CH <sub>3</sub> ) <sub>6</sub>	7.81

<sup>a</sup> Solvent CCl<sub>4</sub>, measured at 430 mμ.

hexamethylbenzene complexes, the acceptor strength is in the order<sup>275</sup>: 1,2,3,5-tetranitrobenzene > 1,3,5-trinitrobenzene > 1,3,4-trinitrobenzene > 1,2,3-trinitrobenzene.

Various relations among the thermodynamic properties,  $\Delta F^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the equilibria of charge-transfer complexes of TNB acceptors have been studied in detail<sup>267, 268</sup>. The charge-transfer energy in TNB aromatic complexes has been correlated with the energy gap found by semiconduction measurements<sup>276</sup>.

The formation of Meisenheimer structures by the reaction of TNB type derivatives with amines and other type of donors may be considered as charge-transfer reactions<sup>173-175</sup>; the formation of such compounds is always associated with colors and marked changes in the electronic absorption spectra<sup>268</sup>.

A crystallographic study of the 1:1 adduct of *p*-iodoaniline and *sym*-TNB has shown that there is alternate stacking of donor and acceptor rings in parallel planes<sup>277</sup>. In solution phase also parallel

orientation of the planes of the aromatic donors and nitroaromatic acceptors is found to occur<sup>278</sup>. The charge-transfer band in TNB-aromatic complexes has been found to be polarized along the intermolecular axis by a study of crystal spectra under polarized radiation<sup>279</sup>. It has been shown that capacity of a  $\pi$ -donor-nitroaromatic complex to exhibit charge-transfer absorption is not greatly affected by changes in the orientation in the compounds with respect to each other<sup>267</sup>.

The TNB complexes in glassy state at low temperatures exhibit emission spectra similar to the phosphorescence spectra of the donors<sup>281</sup>. These emission bands have been found to be the mirror images of the charge-transfer spectra<sup>282</sup>. A detailed discussion of the fluorescence and phosphorescence spectra of these complexes have been given by Briegleb<sup>267</sup>.

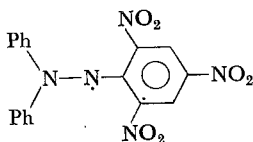
The infrared spectra of weak complexes of aromatics with TNB appear essentially similar to the spectra of the free components, with minute changes in the intensities of the NH absorption in the case of aromatic amine donors<sup>268</sup>. In picric acid-amine salts, the NH frequency of the donor is lowered appreciably while the acceptor OH frequency is also perturbed. In naphthylamine complexes there is little perturbation in the infrared spectra of the complexes<sup>268</sup>.

Some of the recent papers which have appeared in the literature on the charge-transfer interaction of nitro aromatics with various donors are: TNB with aliphatic amines<sup>283, 284</sup>, 2,4,7-trinitrofluorenone aromatic complexes<sup>285</sup>, TNB-acetone system<sup>286</sup>, halide ion-TNB<sup>287</sup>, steric effects on the spectra of nitro- and aminoalkylbenzene complexes<sup>288</sup>, and absolute ultraviolet absorption intensities of the anthracene-trinitrobenzene crystal<sup>289</sup>.

Earlier studies of de Maine<sup>290</sup> indicated that nitromethane interacts with iodine weakly with an equilibrium constant of 1.2 l. mole<sup>-1</sup> at 18°. Bhaskar and Rao<sup>291</sup> have studied the nitro-methane-iodine system in detail and have measured the 1:1 equilibrium constants employing the iodine absorption band. The enthalpy of association has been found to be about 3.0 Kcal/mole. No c.t. band was observed in this system.

## IX. ELECTRON SPIN RESONANCE SPECTRA

The most well known organic free radical which has been investigated by electron spin resonance (esr) spectroscopy is  $\alpha, \alpha$ -diphenyl- $\beta$ -picrylhydrazil (DPPH)<sup>292, 293</sup>;



this radical does not dimerize and gives stable violet crystals. In the esr spectrum (in the solid state), DPPH shows a narrow single line close to the free spin value ( $g = 2.0036$ ) and is often used as a 'g-marker' for calibrating magnetic fields. The nuclear hyperfine structure of DPPH in the esr spectrum has been interpreted in terms of the residence time of the unpaired electron on the two nitrogen nuclei, assuming that the hybridization of the orbitals is the same for the two nitrogen atoms<sup>294-296</sup>. Recently, additional splitting due to the protons attached to the aromatic ring has been observed by careful studies in deoxygenated solutions<sup>297</sup>. The effect of change of the molecular structure of DPPH on the nitrogen hyperfine splitting has been investigated. The various structural changes examined are: presence of an additional bond between the neighboring *ortho*-positions of the 2-phenyl groups<sup>295, 296</sup>, replacement of a nitro group in the picryl ring by a sulfonate ion<sup>295</sup>, radicals with *para*-substituents on the picryl ring and a study of the substituent effects<sup>298</sup>, and mono- and dinitro derivatives of DPPH<sup>299</sup>. Substituent effects including those of the nitro group on benzoyl hydrazyl radicals have also been examined<sup>300</sup>.

Esr spectroscopy has been particularly useful in the study of radical anions<sup>301</sup>. The  $^{14}\text{N}$  hyperfine coupling constants in electrolytically generated radical anions of aliphatic nitro compounds in aqueous solutions have been reported<sup>302</sup> and are listed in Table 20. The lifetime of these anions is fairly long. Solvent effects on the  $^{14}\text{N}$  coupling constants are found to be negligible for the aliphatic nitro anions.

TABLE 20.  $^{14}\text{N}$  hyperfine coupling constants in radical ions of nitroalkanes.

Negative ion radical	$ A_{\text{N}} $ gauss
Nitroethane	25.2
1-Nitropropane	24.8
2-Nitropropane	25.4
1-Nitrobutane	24.3
2-Nitrobutane	24.5

Light induced free radicals in solutions of unsaturated compounds and tetranitromethane have been examined<sup>303</sup>. Two types of free radicals have been identified in the alkali salts of trinitromethane by esr spectroscopy<sup>304</sup>: reduction with dithionite, cysteine, or by electrolytic methods in aqueous solution gives free radicals exhibiting a 7-line spectrum, indicating interaction of the unpaired electron with three equivalent  $^{14}\text{N}$  nuclei. This species is undoubtedly due to the trinitromethane anion radical. An esr spectrum showing five main groups of doublets was obtained when trinitromethane was heated in an alkaline solution of glucose, indicating interaction with two equivalent  $^{14}\text{N}$  nuclei and one proton. This is probably due to the dinitromethane anion radical formed by hydrolytic cleavage. Methyl radical and  $\text{NO}_2$  have been identified in the photolysis of nitromethane while  $\text{NO}_2$  and  $\text{C}(\text{NO}_2)_3$  have been identified in the photolysis of tetranitromethane<sup>305</sup>.

TABLE 21. Isotropic proton and  $^{14}\text{N}$  hyperfine coupling constants for the nitrobenzene anion radicals<sup>306,307</sup>.

Parent compound	$A_{\text{N}}(\text{NO}_2)$	$A_{\text{H}}(2,6)$	$A_{\text{H}}(3,5)$	Other interactions
Nitrobenzene	$\begin{cases} 10.32 \\ 10.33 \end{cases}$	$\begin{cases} 3.39 \\ 3.46 \end{cases}$	$\begin{cases} 1.09 \\ 1.13 \end{cases}$	$\begin{cases} 3.97 \\ [A_{\text{H}}(4)] \\ 3.86 \\ [A_{\text{H}}(4)] \end{cases}$
<i>p</i> -Dinitrobenzene	1.74	1.12	1.12	—
<i>p</i> -Nitroaniline	12.18	3.36	1.12	$\begin{cases} 1.12 \\ [A_{\text{H}}(\text{N})] \end{cases}$
<i>p</i> -Nitroanisole	11.57	3.43	1.11	$\begin{cases} 0.30 \\ (A_{\text{Me}}) \end{cases}$
<i>p</i> -Nitrotoluene	10.79	3.39	1.11	$\begin{cases} 3.98 \\ (A_{\text{Me}}) \end{cases}$
<i>p</i> -Fluoronitrobenzene	10.76	3.56	1.16	$\begin{cases} 8.41 \\ (A_{\text{F}}) \end{cases}$
<i>p</i> -Nitrobenzaldehyde	5.83	$\begin{cases} 3.10 \text{ and} \\ 2.37 \end{cases}$	0.44	$\begin{cases} 1.23 \\ [A_{\text{H}}(\text{HCO})] \end{cases}$
<i>o</i> -Dinitrobenzene	3.22	$\begin{cases} 1.63 \\ [A_{\text{H}}(4,5)] \end{cases}$	$\begin{cases} 0.42 \\ [A_{\text{H}}(3,6)] \end{cases}$	—
<i>m</i> -Dinitrobenzene	4.68	$\begin{cases} 3.11 \\ [A_{\text{H}}(2)] \end{cases}$	$\begin{cases} 4.19 \\ [A_{\text{H}}(4,6)] \end{cases}$	$\begin{cases} 1.08 \\ [A_{\text{H}}(5)] \end{cases}$

A number of *para*-substituted nitrobenzene anion radicals have been studied<sup>306,307</sup> and the total hyperfine coupling to ring protons (*ortho*-, and *meta*- to the  $\text{NO}_2$  group) is found to be constant provided the *meta* coupling is positive. The equation,  $A_o + A_m = -2.3$ , is obeyed in many compounds (Table 21). The  $^{14}\text{N}$  coupling is sensitive

to substitution (12.8 g for *para*-amino and 1.74 g for *para*-nitro). The low coupling in *p*-dinitrobenzene may arise from the flattening of the anion radical<sup>301</sup>, or might be due to the importance of the quinoid structure in the *para*-isomer<sup>306</sup>. The difference between the results of the nitrobenzene radical anions of Maki and Geske<sup>306</sup> and of Ward<sup>307</sup> have been shown to arise from the formation of contact ion pairs<sup>308a</sup>. The splitting constants of a large number of radical ions including those of nitro compounds have been tabulated by Bowers<sup>308b</sup>.

The esr spectra of nitrobenzene and nitrotoluene anions have been examined, along with their optical absorption spectra and the structure of the anions have been calculated in terms of the configuration interaction between the ground state, the locally excited, and the charge-transfer configurations<sup>172</sup>. The  $\sigma$ - $\pi$  parameters for the N—O bonds have been derived from the <sup>14</sup>N hyperfine coupling constants of nitrogen-oxygen radicals and the results have been employed to show that there may be significant deviation from the planarity at the nitrogen atom in aromatic nitro anions<sup>309</sup>; the deviation increases with the increase in the spin density of the nitro group. A marked decrease in the ratio of the anisotropic to the isotropic <sup>14</sup>N coupling has been found in nitroaromatic anions with the increase in spin density and the results are interpreted in terms of the tendency of the nitro group to become pyramidal<sup>310</sup>.

The <sup>17</sup>O isotropic coupling constants in the nitrobenzene ion radical was 8.86 gauss in acetonitrile; in DMF the value was 8.84 and it increased to 8.99 gauss in DMF containing 10 % water<sup>311</sup>. The possibility of considering  $A_o$  in terms of the equation,

$$A_o = Q_1\rho_o^\pi + Q_2\rho_N^\pi$$

has been discussed. The <sup>31</sup>P hyperfine coupling constant in electrolytically produced anion radicals of a number of substituted nitrophenyl phosphates has been determined<sup>312</sup>, and the  $A_P$  varies from 7 to 17.5 gauss.

Study of radical anions of substituted nitrobenzenes in aprotic solvents has shown that these solvents cause marked changes in the electron distribution around the nitrogen atom through hydrogen bonding<sup>313</sup>. The hyperfine interaction, the relaxation time, and the line widths are all affected by the solvent. Solvent effects on the coupling constants in the esr spectrum of nitrobenzene anions have been studied (in DMF-water solutions) and the results are compared



with the results of visible spectra<sup>314</sup>. The esr spectrum of nitrobenzene radical anion has been studied in liquid ammonia<sup>315</sup>.

Spin distribution in *m*-dinitrobenzene anion radical has been found to be affected markedly by the ion pair formation and the nuclear hyperfine interaction has been examined in detail<sup>316,317</sup>. The esr spectra of *p*-dinitrobenzene anions in methanol-dioxane mixtures exhibit marked line width alternation due to the small difference between the isotropic hyperfine coupling of the two nitrogen atoms; some lines were nearly undetectable at low methanol concentrations.<sup>318a</sup>. The mean *N*-hyperfine coupling constant was smaller in dioxane-methanol mixtures than in solvents such as methanol but close to acetonitrile and other poor hydrogen bonding media<sup>318a</sup>. The study of ion pairs (of nitroaromatics) has been discussed by Symons<sup>318b</sup>. Based on the esr spectra of fluoronitrobenzene, evidence has been presented for the steric hindrance of a nitro group when two fluorine atoms are present in the *ortho* position<sup>319</sup>. The  $\pi$ -electron spin densities in 3,5-difluoronitrobenzene anion have been studied<sup>320</sup> and the spectra of nitrochlorobenzene anion radicals have been reported<sup>321</sup>. Steric effects on the anion radicals of nitrobenzene and nitroaniline have been examined by esr spectroscopy along with polarographic results<sup>322a</sup>. When the NO<sub>2</sub> group is twisted out of the plane of the ring the *N*-hyperfine coupling constant increases significantly while the ring proton coupling constant decreases. The problem of line widths and frequency shifts in nitroaromatic anions has been excellently discussed by Fraenkel<sup>322b</sup>. The radical produced by the photolysis of *o*-nitrobenzaldehyde has been examined<sup>323</sup>.

The esr spectra of the radical anion of *s*-trinitrobenzene and related species have been examined in detail<sup>324,325</sup>. The nitro groups in *s*-trinitrobenzene can rotate freely. The anions show alternate line width effects which increase with the interaction of anion and the environment. The influence of various cations on the spectra of trinitrobenzene anions have also been studied<sup>325</sup>. The esr spectra of the radical anions of trinitromesitylene and dinitroindurene, produced electrolytically, have been investigated along with their polarographic behavior by Bernal and Fraenkel<sup>326</sup>. These radicals have been recently shown to be nitroamine anions corresponding to the reduction of one nitro group<sup>327</sup>. Light-induced radicals of *s*-trinitrobenzene in THF show three groups of four lines of relative intensities 1:3:3:1; apparently, the interaction with only one nitrogen nucleus may be due to a complex containing 3 molecules of THF<sup>328</sup>. Some

of the other systems studied recently by esr spectroscopy are: radical ions of *bis-p*-nitrophenyl derivatives of the general formula,  $p\text{-NO}_2\text{C}_6\text{H}_4\text{-X-}p\text{-NO}_2\text{C}_6\text{H}_4$ , where  $\text{X} = \text{O}, \text{S}$  or  $(\text{CH}_2)_2$ <sup>329</sup>, substituted *p*-nitrodiphenyls<sup>330</sup>, dinitrobenzils<sup>331</sup>, nitro-*p*-terphenyls<sup>332</sup>, 9-nitro-triptycene<sup>333</sup>, 5-nitrofuran derivatives<sup>334</sup>, 3-nitropyridine<sup>177</sup>, and the pyrolysis products of nitroaromatic compounds<sup>335</sup>.

## X. MISCELLANEOUS SPECTROSCOPIC STUDIES

The ultraviolet and infrared absorption spectra of nitrobenzene adsorbed on silica gel has been examined and the  $\lambda_{\text{max}}$  of the intramolecular charge-transfer band is found at about 261  $\text{m}\mu$ <sup>336</sup>. The  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  frequencies of the  $\text{NO}_2$  group were identical with those in carbon disulphide solution, but the C—H frequencies showed deviations indicating that the benzene ring is perturbed by the surface. Diffuse reflectance spectroscopy has been employed to examine the reversible photochemical conversion of 2-(2,4-dinitrobenzyl) pyridine in the adsorbed state<sup>337</sup>.

The emission spectrum of detonation waves in nitromethane has been studied<sup>338</sup>. Photochromism of 2-(2-nitro-4-cyanobenzyl)-pyridine in a mixture of ether-isopentane-ethanol (5:5:2 by volume) at liquid nitrogen temperature has been examined<sup>339</sup>.

Stimulated Raman spectrum of nitrobenzene as well as Raman diffusion measurements have been investigated employing laser sources<sup>340, 341</sup>. Two-step Raman scattering in nitrobenzene has also been studied by employing a ruby laser<sup>342</sup>. Resonance Raman effect in a number of nitrobenzene derivatives has been investigated<sup>343</sup>. The relation between the electronic absorption spectra and the Raman spectra of several nitro compounds has been discussed<sup>344, 345</sup>. The infrared transmittance spectrum of nitrobenzene has been analyzed in terms of Kerr coefficients derived from visible and infrared data<sup>346</sup>.

## XI. ACKNOWLEDGMENT

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## CHAPTER 3

# Spectroscopy of the nitroso group

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I. INTRODUCTION . . . . .	137
II. INFRARED ABSORPTION SPECTRA . . . . .	138
A. The N=O Stretching vibration frequency . . . . .	139
1. Organic nitrites . . . . .	139
2. C-Nitroso compounds . . . . .	139
3. Nitrosamines . . . . .	144
B. Other Frequencies of Nitroso Compounds . . . . .	146
III. ELECTRONIC ABSORPTION SPECTRA . . . . .	147
A. C-Nitroso Compounds . . . . .	148
B. Nitrosamines . . . . .	152
IV. NUCLEAR MAGNETIC RESONANCE SPECTRA . . . . .	155
V. ELECTRON SPIN RESONANCE SPECTRA . . . . .	160
VI. MICROWAVE SPECTRA . . . . .	161
VII. REFERENCES . . . . .	161

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## I. INTRODUCTION

Organic compounds containing the  $R-N=O$  unit may exist as nitrites,  $-O-N=O$ , nitroso compounds,  $-C-N=O$ , or nitrosamines,  $-N-N=O$ , and the spectroscopy of the last two classes of compounds will form the subject matter of this chapter. Wherever necessary reference will be made to the spectroscopy of organic nitrites and other related systems. In recent years, a fairly large number of publications have appeared in the literature on the spectroscopy of nitroso compounds. Spectroscopic methods have

been particularly valuable in the study of the stereochemistry, restricted rotation and dimerization of nitroso compounds and many of the earlier controversies regarding the interpretation of the spectra seem to have been clarified. In this chapter, the spectroscopy of nitroso compounds will be reviewed exhaustively in the light of the more recent publications in the literature.

## II. INFRARED ABSORPTION SPECTRA

The infrared spectra of nitroso compounds have been briefly reviewed by some authors<sup>1-3</sup>. The most important group frequency of interest in these derivatives is due to the N=O stretching vibration. Before discussing the infrared spectra of organic nitroso compounds containing the R—N=O unit, it may be relevant to briefly summarize the available information on the N=O stretching frequencies in inorganic derivatives<sup>4</sup>.

Nitric oxide, NO, exists as a dimer in the condensed state at low temperatures and the NO stretching frequencies have been found at 1883 (monomer), 1862 and 1768 (*cis*-dimer) and 1740 cm<sup>-1</sup> (*trans*-dimer). Nitrosonium ion, on the other hand, gives characteristic absorption in the triple bond region (2150–2400 cm<sup>-1</sup>). Nitrosyl halides show the characteristic N=O stretching frequency in the region 1799–1845 cm<sup>-1</sup>, the frequency being highest in the case of nitrosyl fluoride. In coordination compounds, the N=O group may be cationic (NO<sup>+</sup>), anionic (NO<sup>-</sup>) or nearly neutral (NO), depending on the nature of the metal ion and the other ligand. The cationic stretching frequency is found to be in the range 1575–1940 cm<sup>-1</sup> while the anionic frequency is between 1040 and 1200 cm<sup>-1</sup>. In some coordination compounds, bridging N=O groups have been found to give rise to bands around 1500 cm<sup>-1</sup>. Thus in inorganic compounds the N=O stretching frequency shows large variations covering a wide range of frequencies anywhere between 1040 and 1940 cm<sup>-1</sup>. This is a much wider range than that found in carbonyl compounds.

The N=O stretching frequencies in organic compounds containing the R—N=O unit are found in a much narrower range than in inorganic compounds. The general range for the N=O frequency in the organic derivatives is 1400–1690 cm<sup>-1</sup>. Since many of the nitroso compounds undergo dimerization, stretching frequencies corresponding to the N=O bond are seen in the dimers in the range 1000–1450 cm<sup>-1</sup>.

## A. The N=O stretching vibration frequency

### 1. Organic nitrites R—O—N=O

Organic nitrites show a doublet absorption band in the region 1610–1685  $\text{cm}^{-1}$  due to the N=O stretching vibration<sup>2,3</sup>. The doublet is due to the *trans* and *cis* forms of the nitrites, the *trans* isomer absorbing at higher frequencies (1650–1685  $\text{cm}^{-1}$ ) than the *cis* isomer (1610–1625  $\text{cm}^{-1}$ )<sup>4-7</sup>. The stretching frequency in nitrites decreases with the increasing bulk of the attached group. Thus, methyl nitrite shows the absorption bands at 1625 and 1681  $\text{cm}^{-1}$ , while amyl nitrite shows these bands at 1613 and 1653  $\text{cm}^{-1}$ . The band positions are also affected by the electronegativities of the substituents. Accordingly, trifluoroethyl nitrite absorbs at 1736 (*trans*) and 1695  $\text{cm}^{-1}$  (*cis*).

The ratio of the *cis* and *trans* forms varies with substitution and the proportions can be readily estimated by the measurement of the extinction coefficients of the *trans* and the *cis* bands. The *trans* to *cis* ratios are found to be 1:1 in methyl nitrite, 2:3 in ethyl nitrite and 3:3.5 in higher primary nitrites. In the secondary nitrites, the ratio is 6:10 while in tertiary nitrites it is 40:1. Apparently the *cis* form is not favored in the tertiary derivatives.

The infrared spectrum of methyl thionitrite,  $\text{CH}_3\text{—S—NO}$ , has been reported recently<sup>8</sup>, and the N=O stretching frequency in this compound is found at 1534  $\text{cm}^{-1}$ .

### 2. C-Nitroso compounds

Thompson and coworkers<sup>9</sup> proposed the 1300–1400  $\text{cm}^{-1}$  range for the N=O stretching frequency in nitroso compounds, while Brownlie<sup>10</sup> suggested 1650  $\text{cm}^{-1}$  for the same absorption. The wide difference in the frequency ranges quoted for the nitroso group arises from the dimerization and the geometrical isomerism in the nitroso compounds. Recent studies of Lüttke<sup>11-13</sup>, Tarte<sup>14</sup> and Gowenlock and coworkers<sup>15</sup> have clarified the difficulties regarding the assignment of the N=O stretching absorption frequency and the important results will be summarized in the following paragraphs.

It is possible to identify the free N=O stretching vibrations of monomeric nitroso compounds in vapor state or in dilute solutions. In nitrosomethane and nitrosocyclohexane, the monomeric bands are found at 1564 and 1558  $\text{cm}^{-1}$ , respectively in the vapor state

while in solution both compounds exist mainly as dimers. Aromatic nitroso compounds generally show the free  $\text{N}=\text{O}$  stretching vibration in the region of  $1485\text{--}1515\text{ cm}^{-1}$ , while in aliphatic compounds (including halogenated derivatives) the region is  $1538\text{--}1621\text{ cm}^{-1}$ . The positions of the monomeric  $\text{N}=\text{O}$  stretching frequency in a number of C-nitroso compounds are shown in Table 1.

TABLE 1. Monomeric  $\text{N}=\text{O}$  stretching frequencies of C-Nitroso compounds<sup>11,16</sup>

Aliphatic	$\nu_{\text{N}=\text{O}}, \text{cm}^{-1}$	Aromatic	$\nu_{\text{N}=\text{O}}, \text{cm}^{-1}$
Nitrosomethane	1564	Nitrosobenzene	1506
Trifluoronitrosomethane	1595	<i>p</i> -Fluoronitrosobenzene	1511
Trichloronitrosomethane	1621	<i>p</i> -Chloronitrosobenzene	1500
1,1-Dichloro-1-nitroso-ethane	1598	<i>p</i> -Bromonitrosobenzene	1497
2-Chloro-2-nitrosopropane	1587	<i>p</i> -Iodonitrosobenzene	1488
2-Nitro-2-nitrosopropane	1585	<i>p</i> -Methylnitrosobenzene	1508
2-Cyano-2-nitrosopropane	1570	<i>p</i> -Methoxynitrosobenzene	1497
2-Methyl-2-nitrosopropane	1546	<i>p</i> -Nitronitrosobenzene	1513
2-Acetyl-2-nitrosopropane	1539	<i>m</i> -Nitronitrosobenzene	1504
Heptafluoro-1-nitroso-propane	1603	<i>m</i> -Nitrosomitrosobenzene	1511
Nitrosocyclohexane	1558	3,5-Dichloronitrosobenzene	1502
1-Chloro-2-nitrosocyclohexane	1572	<i>o</i> -Methylnitrosobenzene	1499
1,4-Dichloro-1,4-dinitrosocyclohexane ( <i>trans</i> form)	1570	<i>o</i> -Nitronitrosobenzene	1511
1-Chloro-1'-nitrosodicyclohexyl	1555	<i>o</i> -Methoxynitrosobenzene	1495
9-Chloro-10-nitrosodecaline	1555	<i>o</i> -Iodonitrosobenzene	1502
		Nitrosomesitylene	1495
		2,4,6-Tribromonitrosobenzene	1506

In aliphatic nitroso compounds, substitution of an  $\alpha$ -hydrogen by an acetyl group lowers the  $\text{N}=\text{O}$  frequency whereas substitution by a Cl, CN or  $\text{NO}_2$  group increases the frequency<sup>1</sup>. Di- and trisubstitution leads to higher frequencies of the  $\text{N}=\text{O}$  stretching absorption in aliphatic compounds. In this respect, the behavior of the  $\text{N}=\text{O}$  group is different from that of the  $\text{C}=\text{O}$  group. It is possible that resonance interaction involving double bonded carbon-halogen bonds play an important role in the nitroso compounds.

O'Sullivan and Sadler<sup>17</sup> have found a linear correlation between the  $\text{N}=\text{O}$  stretching frequencies in compounds of the general formula



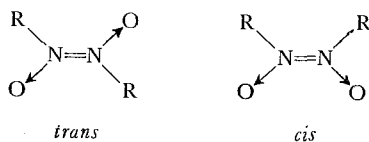
RNO and the aliphatic polar substituent constants of Taft. The relations are expressed as:

$$\nu = 1500 + 110\sigma^* \text{ (vapor phase)}$$

$$\nu = 1458 + 124\sigma^* \text{ (condensed phase)}$$

The substituent effects in aromatic compounds are found to be small and the frequencies can be understood in terms of the Hammett substituent constants. The N=O stretching frequency is enhanced due to field effects in cyclohexane derivatives just as in the case of carbonyl compounds. Thus, 1,4-dichloro-1,4-dinitrosocyclohexane absorbs at  $1570 \text{ cm}^{-1}$  compared to nitrosocyclohexane which absorbs at  $1558 \text{ cm}^{-1}$ .

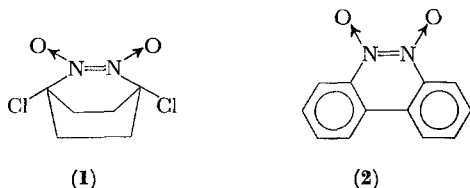
The intensity of the bands ascribed to the N=O stretching vibrations in C-nitroso compounds vary with temperature as well as dilution<sup>18,19</sup>. For example, the intensity of the  $1475 \text{ cm}^{-1}$  band of nitrosomesitylene decreases with increase in temperature and two new bands appear at  $1490$  and  $1400 \text{ cm}^{-1}$ . The intensity of the  $1475 \text{ cm}^{-1}$  band also decreases on dilution giving rise to a higher intensity of the other two bands. These results clearly show that the variation in the band intensities is associated with the monomer-dimer equilibrium in this compound. Detailed studies have clearly shown that most C-nitroso compounds exist predominantly in the dimeric form. The investigations of Gowenlock, Spedding, Trotman and Whiffen<sup>15</sup> have shown that the dimeric structure of the nitroso compounds can have either the *cis* or the *trans* configuration. This geometrical isomerism becomes possible because of the appreciable



double-bond character of the N—N bond in the dimer. The absorption of the *cis* and *trans* dimers, (RNO)<sub>2</sub> are summarized below<sup>1</sup>:

R	<i>trans</i> -dimer	<i>cis</i> -dimer
Aliphatic	Single band between $1176$ and $1290 \text{ cm}^{-1}$	Two bands in the regions $1323$ – $1344$ and $1330$ – $1420 \text{ cm}^{-1}$
Aromatic	Single band between $1253$ and $1299 \text{ cm}^{-1}$	Two bands in the regions $1389$ – $1397$ and $1409 \text{ cm}^{-1}$

The assignment of the *cis* dimer bands has been justified by examination of the N=O stretching absorption in compounds **1** and **2**:



Raman studies of dimeric nitrosocyclohexane (*trans*) and nitrosobenzene (*cis*) also lend support to these assignments<sup>20</sup>.

The intensities of the bands of the *cis* and *trans* dimers are considerably different<sup>15</sup>. The *trans* dimers generally show high intensity bands ( $\epsilon \sim 600 - 1500$ ) in the region  $1190-1300\text{ cm}^{-1}$ , while the *cis* dimers do not show any bands in this region with  $\epsilon > 80$ . Band intensity data on the *cis* and *trans* dimers of a few nitroso derivatives are shown in Tables 2 and 3. On the basis of the band intensities, it is possible to assign *cis* and *trans* structures to unknown dimers<sup>15</sup>.

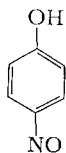
The dimer band intensity in *para* substituted nitrosobenzenes increases with the electron withdrawing ability of the *para* substituent<sup>19</sup>. The stability of the aromatic dimers also depends on the substituents<sup>18</sup>. Thus, nitrosomesitylene exists only as a dimer while the *para*-dimethylamino- and *para*-iodonitrosobenzenes exist essentially as monomers even in the solid state. Apparently, electron-donating groups weaken the N=N band in the dimer and hence lower the stability. The *cis* dimers are generally more stable in phenyl derivatives and conjugation between the two benzene rings is decreased in these dimers.

In nitroso dimers, the bond order of the nitrogen-oxygen bond is no longer two and it would be worthwhile comparing the N→O stretching frequencies of the nitroso dimers with those of amine oxides and related derivatives<sup>3</sup>. The characteristic absorption of the N→O linkage in amine oxides is found in the  $1200-1310\text{ cm}^{-1}$  region and the position of the band is sensitive to the electrical properties of substituents. Thus, *p*-methoxypyridine-N-oxide absorbs at  $1238\text{ cm}^{-1}$  compared to the *p*-nitro derivative which absorbs at  $1304\text{ cm}^{-1}$ . Azoxy compounds show the N→O absorption in the  $1250-1310\text{ cm}^{-1}$  region and nitriloxides,  $\text{R}-\text{C}\equiv\text{N}\rightarrow\text{O}$ , show the N→O absorption in the  $1340-1380\text{ cm}^{-1}$  range.

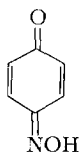
Some nitroso compounds show evidence of oxime formation in their infrared spectra<sup>11</sup>. For example, the N=O stretching bands

R	$\nu_i$ , cm <sup>-1</sup>	$\varepsilon$	$\nu_{ii}$ , cm <sup>-1</sup>	$\varepsilon$	$\nu_{iii}$ , cm <sup>-1</sup>	$\varepsilon$	$\nu_{iv}$ , cm <sup>-1</sup>	$\varepsilon$	$\nu_{vi}$ , cm <sup>-1</sup>	$\varepsilon$
Me	1387	300	1341	60	—	—	1107	40	1061 1017	30 200
Et	1426 1370	80 90	1323	30	1290	40	1078	50	1043	90
<i>n</i> -Bu	1426 1385	100 150	1336	50	1296	30	1096	70	1041	150
<i>i</i> -Bu	1418 1382	40 70	1338	30	1304 1287	20 30	1095	50	1039	80
<i>s</i> -Bu	1420 1384	80 100	1338	50	1296	40	1096	50	1040	100
<i>s</i> -C <sub>5</sub> H <sub>11</sub>	1408 1377	150 130	1323	90	1306	40	1087	80	1045 1031	40 60

important bands due to the oxime unit in a number of such derivatives<sup>22,23</sup>.



(3)



(4)

2-Nitrosophenol has been found to exist in the chelated form both in solid state and in solution<sup>24</sup>. The O—H stretching frequency is not seen in 1-nitroso-2-naphthol. The quinone monoxime structures are probably stabilized in the chelates of these compounds.

### 3. Nitrosamines

In the monomeric state nitrosamines show the N=O stretching absorption in the region  $1430\text{--}1530\text{ cm}^{-1}$ . Dimers generally absorb in the  $1300\text{ cm}^{-1}$  region<sup>6,7,14,25,26</sup>. The N=O stretching frequency of nitrosamines is appreciably higher in vapor phase compared to that in solution phase. Thus, in dialkyl nitrosamines the N=O stretching frequency is around  $1490\text{ cm}^{-1}$  in vapor and around  $1450\text{ cm}^{-1}$  in  $\text{CCl}_4$  solution. Some infrared data on the nitrosamines are given in Figure 1 and Table 4.

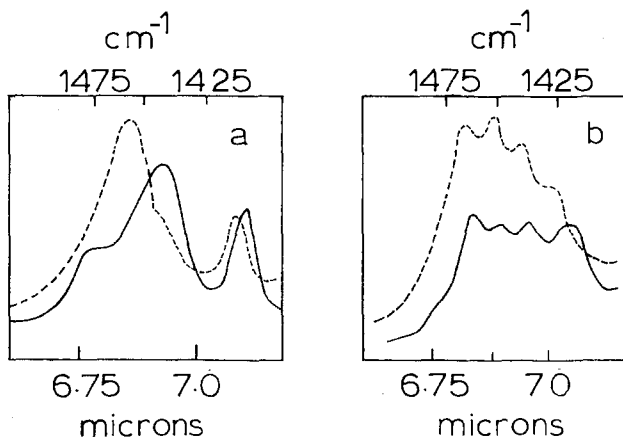


FIGURE 1. Infrared spectra in the N=O stretching region of (a) dimethylnitrosamine and (b) diethylnitrosamine in carbon tetrachloride (dotted line) and in methylene bromide (full line).

TABLE 4. Major infrared bands of nitrosamines in  $\text{CCl}_4$  solvent<sup>30</sup>.

Compound	$\nu_{\text{NO}}$ , $\text{cm}^{-1}$	$\nu_{\text{CN}}(\text{aromatic})$ , $\text{cm}^{-1}$	$\nu_{\text{NN}}$ , $\text{cm}^{-1}$
Dimethylnitrosamine	1460		1035
Diethylnitrosamine	1454		1060
Diisopropylnitrosamine	1438		1139
<i>N</i> -nitrosopiperidine	1437		1087
Dicyclopentylnitrosamine	1444		1112
Dicyclohexylnitrosamine	1442		1112
<i>N</i> -nitrosomethylaniline	1476	1194	944
<i>N</i> -nitrosoethylaniline	1478	1175	993
<i>N</i> -nitrosocarbazole	1478		1051
<i>N</i> -nitrosodiphenylamine	1480		1038

The position of the  $\text{N}=\text{O}$  stretching band of nitrosamines is affected by the electronegativity of substituents. In *N*-nitroso-bis-2,2,2-trifluoroethylamine, the  $\text{N}=\text{O}$  stretching frequency is at  $1550\text{ cm}^{-1}$ <sup>7</sup>. In *N*-nitrosamides the absorption is found in the region  $1515\text{--}1530\text{ cm}^{-1}$ <sup>27</sup>. In nitrosoguanidines, the  $\text{N}=\text{O}$  stretching frequencies are found in the region  $1500\text{--}1600\text{ cm}^{-1}$ <sup>28</sup>. Sydnones do not show the nitroso absorption<sup>25</sup>.

The infrared stretching frequency of the nitroso groups in nitrosamines has been correlated with the polarographic half-wave potentials as well as rates of hydrolysis in acidic media<sup>29</sup>.

The solvent effects on the aliphatic and aromatic nitrosamines have been examined by Williams and coworkers<sup>30</sup>, who have made use of such effects to assign some of the vibrations of the  $\text{N}-\text{N}=\text{O}$  group. Aliphatic nitrosamines show a band in the  $1425\text{--}1460\text{ cm}^{-1}$  region associated with the  $\text{N}=\text{O}$  stretching vibration. Its intensity decreases and moves to lower frequencies on going from carbon tetrachloride to methylene dibromide solution. Aromatic nitrosamines, which show the  $\text{N}=\text{O}$  stretching frequency in the region  $1500\text{--}1450\text{ cm}^{-1}$ , also show similar solvent sensitivity. Solvent effects on the characteristic bands of nitrosamines can be seen in Table 5 and Figure 1. Coupling between the  $\text{N}=\text{O}$  stretching vibration and the  $\text{CH}_2$ ,  $\text{CH}_3$  bending modes or the ring  $\text{C}-\text{C}$  vibration is encountered in the aromatic nitrosamines<sup>30</sup>.

The infrared spectra of the dimer of trifluoronitrosomethane indicates that it has the nitritoamine structure,  $(\text{CF}_3)_2\text{N}-\text{O}-\text{N}=\text{O}$ <sup>31</sup>. The  $\text{N}=\text{O}$  stretching bands of the dimer were found at  $1803$  and  $1830\text{ cm}^{-1}$ , nearly  $200\text{ cm}^{-1}$  higher than the frequencies normally found for nitroso compounds and nitrites.

TABLE 5. Solvent effects on the infrared frequencies ( $\text{cm}^{-1}$ ) of dimethylnitrosamine<sup>30</sup>.

Solvent							
Vapor		1489	1412		1310	1294	1016
Liquid	1480	1448	1413	1396	1321	1293	1053
Carbon tetrachloride	1477	1460	1411	1394	1313	1292	1023
Benzene	1481	1453	1411	1394	1313	1292	1037
Methylene chloride	1478	1446	1408	1392	1319	1292	1051
Chloroform	1478	1444	1408	1392	1321	1292	1051
Methylene bromide	1476	1444	1408	1392	1318	1291	1049
Methylene iodide	1473	1441	1404	1390	1315	1289	1049

The infrared spectra of nitrosohydroxylamine derivatives show the  $\text{N}=\text{O}$  stretching bands at 1246–1286 and 1174–1242  $\text{cm}^{-1}$  and the  $\text{N}-\text{N}$  stretching frequency at 910–980  $\text{cm}^{-1}$ <sup>32</sup>. Infrared data on some nitrosopiperazines and the alkylation products of nitrosohydroxylamines (the so-called diimide dioxides) have been reported in the literature<sup>33</sup>.

The  $\text{N}=\text{O}$  stretching frequency in addition compounds of dialkyl nitrosamines with metal as well as non-metal halides have been reported recently<sup>34</sup>.

### B. Other Frequencies of Nitroso Compounds

In alkyl nitrites, the  $\text{O}-\text{N}=\text{O}$  bending vibrations of the *cis* and *trans* forms are found in the regions 617–691 and 565–625  $\text{cm}^{-1}$ , respectively<sup>5</sup>. Combination bands have been found in the region 2250–2300 ( $\nu_{\text{N}=\text{O}} + \sigma_{\text{O}-\text{N}=\text{O}}$ ) and at  $\sim 2500$  ( $\nu_{\text{N}=\text{O}} + \nu_{\text{N}-\text{O}}$ )  $\text{cm}^{-1}$ . The first overtone of the  $\text{N}=\text{O}$  stretching vibration is found at 3200–3300  $\text{cm}^{-1}$ .

In the case of C-nitroso compounds there are not many other correlations available, although the  $\text{C}-\text{N}$  stretching vibration has been assigned to a broad band around 1100  $\text{cm}^{-1}$ <sup>11, 14</sup>. The  $\text{C}-\text{N}$  stretching vibration in many of the C-nitroso compounds is probably coupled with other vibrations as suggested by Lüttke who finds contribution from  $\text{C}-\text{N}$  stretching vibration in the bands near 1100 and  $800 \pm 50$   $\text{cm}^{-1}$ . The  $\text{C}-\text{N}=\text{O}$  bending vibration is assigned to a band in the 400–460  $\text{cm}^{-1}$  region<sup>11</sup>.

In nitrosamines, the  $\text{N}-\text{N}$  stretching vibration has been assigned to a band around 1000  $\text{cm}^{-1}$ <sup>6, 7, 14</sup>. Solvent effect studies<sup>30</sup> have shown that the  $\text{N}-\text{N}$  stretching vibration is in the region 1030–1150  $\text{cm}^{-1}$  in aliphatic nitrosamines which shifts to higher frequencies in polar

solvents. In aromatic nitrosamines the N—N stretching vibration has been assigned to a band in the region  $925\text{--}1025\text{ cm}^{-1}$  and the C—N stretching vibration to a band in the region  $1160\text{--}1200\text{ cm}^{-1}$ . The N—N=O deformation mode gives rise to a band around  $660\text{ cm}^{-1}$ <sup>14</sup>.

### III. ELECTRONIC ABSORPTION SPECTRA

The nitro group exhibits a strong absorption band around  $210\text{ m}\mu$  ( $\epsilon \sim 10000$ ) and a weak band around  $270\text{ m}\mu$  ( $\epsilon \sim 20$ ). These bands are most probably due to the  $\pi \rightarrow \pi^*$  and the  $n \rightarrow \pi^*$  transitions, respectively. Another  $n \rightarrow \pi^*$  transition should occur at very low wavelengths, probably in the vacuum ultraviolet region, but this has not been observed. Alkyl nitrites also exhibit weak bands with fine structure due to  $n \rightarrow \pi^*$  transitions around  $350\text{ m}\mu$  ( $\epsilon \sim 80$ ). The electronic spectra of the nitro group have been reviewed in the literature<sup>35</sup>, as well as in Chapter 2. Although there has been considerable amount of published work on the electronic absorption spectra of nitroso compounds, the subject has not been reviewed. Presently, the ultraviolet and visible absorption spectra of nitroso compounds will be discussed; it is outside the scope of this review to discuss the use of nitroso compounds such as 1-nitroso-2-naphthol as colorimetric reagents in analysis.

The monomeric aliphatic nitroso compounds are blue in color while the aromatic derivatives are green in color. The aliphatic monomers show a low intensity absorption maximum in the region of  $630\text{--}790\text{ m}\mu$  ( $\epsilon \sim 1\text{--}20$ ), another absorption maximum in the  $270\text{--}290\text{ m}\mu$  region ( $\epsilon \sim 80$ ), and a fairly intense band around  $220\text{ m}\mu$  ( $\epsilon \sim 5000$ )<sup>1</sup>. Both the low intensity bands around  $700$  and  $300\text{ m}\mu$  are undoubtedly due to  $n \rightarrow \pi^*$  transitions. Of these, the visible absorption band has been assigned to the singlet-singlet transition of the lone-pair on nitrogen, while the lower wavelength  $n \rightarrow \pi^*$  transition has been considered to be due to the oxygen lone-pair<sup>1,36</sup>. Since dimerization of nitroso compounds involves bond formation by the nitrogen lone-pair, the long wavelength  $n \rightarrow \pi^*$  transition is affected markedly and the extinction varies with concentration and temperature. Oxidation of a nitroso compound to a nitro compound is similarly associated with the disappearance of the visible absorption. In aromatic compounds, only the long wavelength  $n \rightarrow \pi^*$  transition is seen distinctly and the lower wavelength  $n \rightarrow \pi^*$  transition is usually submerged in the

aromatic absorption bands. Both the  $n \rightarrow \pi^*$  transitions are characterized by blue-shifts in polar solvents<sup>35,37</sup>. The low wavelength band around 220 m $\mu$  in aliphatic nitroso compounds arises from the  $\pi \rightarrow \pi^*$  transition of the nitroso group.

Dichroism studies on *m*-nitronitrosobenzene has confirmed the assignment of the  $n \rightarrow \pi^*$  transition for the visible absorption band of nitroso compounds<sup>38</sup>. For the 750 m $\mu$  band of *m*-nitronitrosobenzene monomer, the perpendicular absorption is hyperchromic to the parallel absorption indicating that the green color is due to the electronic transition polarized perpendicular to the C—N=O bond<sup>39,40</sup>.

Flash photolysis of *t*-butylnitrite has been found to give nitrosomethane which has been identified by its  $n_N \rightarrow \pi^*$  transition<sup>41</sup>. In the excited state, the C—N=O angle is larger by about 8°. The unusual vibrational features of this spectrum has been interpreted in terms of a decrease in the barrier to torsion of the methyl group, from about 940 cm<sup>-1</sup> in the ground state to about 240 cm<sup>-1</sup> in the excited state.

The electronic structures and electronic spectra of 1-chloro-1-nitrosocyclohexane, nitrosyl chloride, methyl nitrite and *N,N*-dimethylnitrosamine have been studied by Nagakura and co-workers<sup>42</sup> who have carried out molecular orbital calculations. In 1-chloro-1-nitrosocyclohexane, the  $n \rightarrow \pi^*$  transition of the nitroso group is found around 750 m $\mu$  while the  $\pi \rightarrow \pi^*$  transition appears around 160 m $\mu$ . In nitrosyl chloride, the  $n \rightarrow \pi^*$  transition is at 615 m $\mu$  while the  $\pi \rightarrow \pi^*$  transition is found around 145 m $\mu$ . In methyl nitrite and *N,N*-dimethylnitrosamine, the  $n \rightarrow \pi^*$  transitions are found at 386 and 377 m $\mu$ , respectively. In all these compounds, intramolecular charge-transfer bands are found in the region of 197–227 m $\mu$ . It is interesting that the band due to the  $n \rightarrow \pi^*$  transition in these compounds is shifted to shorter wavelengths with increasing electron-donating power of the substituent, while the charge-transfer band is shifted to longer wavelengths. A similar behavior is also seen in carbonyl compounds.

### A. C-Nitroso Compounds

In aromatic nitroso compounds, the  $n_N \rightarrow \pi^*$  transition is found at longer wavelengths than in aliphatic derivatives due to delocalization<sup>43</sup>. The observed bands in the electronic spectra of nitrosobenzene are given at top of facing page<sup>43</sup>.



$\lambda_{\text{max}}, \text{m}\mu$	$\epsilon$
680-760	40-70
301-350	5200
280	10330
194	11890
174	45000

The 300  $\text{m}\mu$  band shows solvent red-shifts<sup>35</sup> and increase in intensity with increase in the polarity of the solvents. The 280  $\text{m}\mu$  as well as the 300  $\text{m}\mu$  bands have been ascribed to charge-transfer from benzene to the nitroso group<sup>43</sup>. The electron withdrawing power of the nitroso group is expected to be greater than that of the nitro group.

When a dimer is formed, the  $n \rightarrow \pi^*$  band disappears and a new  $\pi \rightarrow \pi^*$  transition appears in the region of 270  $\text{m}\mu$  ( $\epsilon \sim 10000$ ), as seen in aliphatic compounds<sup>44</sup>. The color of the compound also changes from blue to yellow. A number of nitrosoalkanes have been prepared by pyrolysis of alkyl nitrites and the *cis* dimers have been isolated in all the cases except in 2-methyl-2-nitrosopropane where only the *trans* dimer is possible due to steric considerations. This study clearly indicates the existence of *cis-trans* isomerism in dimeric nitrosoalkanes. The ultraviolet spectral data of the derivatives have been recorded in water, ethanol, diethyl ether and carbon tetrachloride<sup>44</sup> and the data are summarized in Table 6. The *trans* dimer of 2-methyl-2-nitrosopropane dissociates in organic solvents giving rise to the blue monomer (695  $\text{m}\mu$ ). The 270  $\text{m}\mu$  band of the *trans* isomers shows solvent blue-shifts which are larger in magnitude than those of the *cis* isomers. Further, the wavelength of absorption is always lower in the *cis* isomers than in the *trans* isomers.

The dependence of the long wavelength bands of the monomers on substitution and temperature has been investigated<sup>45</sup>. The enthalpies of dimerization of the nitroso compounds, RNO, calculated on the basis of the temperature dependence of the visible absorption band are given in Table 7.

In aromatic nitroso compounds, the *cis* form of the dimers is more stable and delocalization is inhibited by the twisting of the aromatic rings out-of-plane. The *trans* isomer has not been isolated in the case of nitrosobenzene. In *ortho*-substituted aromatic nitroso dimers, however, the *trans* form is stable since the aryl groups are twisted out-of-plane. The extinction of the visible absorption band is low in aromatic compounds where the resonance interaction is weak

TABLE 6. Solvent effects on the ultraviolet absorption spectra of dimeric nitrosoalkanes<sup>44</sup>, (RNO)<sub>2</sub>.

<i>R</i>	H <sub>2</sub> O		EtOH		Et <sub>2</sub> O		CCl <sub>4</sub>	
	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$
<i>cis</i> -Me	265	4.00	269	4.00	286	—	291	—
<i>trans</i> -Me	276	4.03	282.5	4.01	286	4.01	291	4.06
<i>cis</i> -Et	266	4.02	272	3.94	288	3.87	292	4.00
<i>trans</i> -Et	277	—	285	—	288	—	292	—
<i>cis</i> - <i>n</i> -Pr	268	4.04	273	3.98	291	3.96	295	4.03
<i>trans</i> - <i>n</i> -Pr	280	—	287	—	291	—	295	—
<i>cis</i> - <i>i</i> -Pr	267	4.02	273	3.87	290	3.90	295	4.00
<i>trans</i> - <i>i</i> -Pr	280	4.01	286	3.98	290	3.95	295	4.00
<i>cis</i> - <i>n</i> -Bu	268	4.06	273	3.87	291	3.94	296	4.00
<i>trans</i> - <i>n</i> -Bu	282	—	289	—	291	—	296	—
<i>cis</i> - <i>i</i> -Bu	270	4.04	276	4.00	294	3.96	298	4.02
<i>trans</i> - <i>i</i> -Bu	285	4.01	291	3.98	294	3.96	298	4.02
<i>cis</i> - <i>s</i> -Bu	269	4.02	275	3.95	293	3.89	297	4.01
<i>trans</i> - <i>s</i> -Bu	284	—	290	—	293	—	297	—
<i>trans</i> - <i>t</i> -Bu	287	—	—	—	295 <sup>a</sup>	—	—	—
					675			
<i>cis</i> -C <sub>5</sub> H <sub>11</sub>	271	3.98	278 <sup>b</sup>	3.86	297	3.91	300	4.01
<i>trans</i> -C <sub>5</sub> H <sub>11</sub>	287	—	294	—	297	—	300	—

<sup>a</sup> 295 m $\mu$  absorption peak decreases with time while the 675 m $\mu$  peak increases.<sup>b</sup> Changes very rapidly to give  $\lambda_{\max}$  at 294 m $\mu$ .TABLE 7. Visible absorption data and enthalpies of dimerization of nitroso compounds (RNO)<sup>45</sup>.

<i>R</i>	$\lambda$ , m $\mu$	$\Delta H$ , kcal/mole <sup>a</sup>
C <sub>6</sub> H <sub>5</sub>	755	<10
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	758	<10
<i>p</i> -IC <sub>6</sub> H <sub>4</sub>	758	<10
<i>o</i> -IC <sub>6</sub> H <sub>4</sub>	777	<10
<i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	775	<10
2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	775	10.9
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	797	12.1
MeCOMe <sub>2</sub> C	691	18.9
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	678	20.4
C <sub>6</sub> H <sub>11</sub>	690	20.6

<sup>a</sup> For dissociation of dimers

due to steric effects, but increases on heating or dilution<sup>46</sup>. The monomer-dimer equilibria of a series of 2,6-dichloro-4-substituted-nitrosobenzenes have been studied in benzene solvent and electron-releasing substituents have been found to favor dissociation of the dimers to monomers<sup>47</sup>.

Burawoy<sup>48</sup> has examined the electronic spectra of a few aromatic nitroso compounds and finds that the  $\pi \rightarrow \pi^*$  transitions of the aromatic are shifted to longer wavelengths by *o*-methoxy groups, while the  $n \rightarrow \pi^*$  transitions of the nitroso group are shifted to shorter wavelengths. The NMe<sub>2</sub> group causes a much greater hypsochromic shift of the  $n \rightarrow \pi^*$  transition. Polar solvents shift the  $\pi \rightarrow \pi^*$  transition to longer wavelengths and the  $n \rightarrow \pi^*$  transition to shorter wavelengths in these compounds.

The ultraviolet spectrum of nitrosotropolone has been reported in the literature<sup>49</sup>. The visible absorption has been made use of to characterize *o*-nitroso benzamide as an intermediate in the von Richter reaction<sup>50</sup>.

The  $n \rightarrow \pi^*$  transitions of *para*-substituted nitrosobenzenes, *p*-RC<sub>6</sub>H<sub>4</sub>NO, have been correlated with the polarographic reduction potentials<sup>51</sup> and some of the data are given in Table 8.

TABLE 8.  $n \rightarrow \pi^*$  Absorption data and polarographic reduction potentials of *p*-substituted nitrosobenzenes<sup>51</sup>.

<i>R</i>	$\lambda_{\max}$	$E_{0.5}$ , mv
CHO	760	417
NO <sub>2</sub>	780	430
Cl	748	469
Br	748	471
H	745	479
I	743	485
Me	735	525
MeO	714	598
OH	697	632

Electronic spectra of nitrosophenols have clearly shown that these compounds exist in the quinoid structure<sup>23,52</sup>. Nitrosonaphthols also exist as quinone monoximes<sup>53</sup>. The dissociation constant of 1-nitroso-2-naphthol has been determined by a spectrophotometric method employing the pH dependence of the 380 m $\mu$  band<sup>54</sup>.

The electronic spectra of 2-nitrosophenol, 5-methoxy-2-nitrosophenol and 5-dimethylamino-2-nitrosophenol have been studied in various solvents and compared with the spectra of the corresponding anisoles by Burawoy<sup>55</sup>. The results show that the nitroso group in these phenols forms an intramolecular hydrogen bond causing a shift of the  $n \rightarrow \pi^*$  band to shorter wavelengths. Solvent effect studies also confirm this observation. The positions of the bands of 2-nitrosophenol in a few solvents are given in Table 9.

There appears to be little doubt that 2-nitrosophenol exists truly as a nitroso compound, although it is not possible to exclude the

TABLE 9. Solvent effects on the electronic absorption spectrum of 2 nitrosophenol<sup>55</sup>.

Solvent	$n \rightarrow \pi^*$ band		$\pi \rightarrow \pi^*$ band		$\pi \rightarrow \pi^*$ band	
	$\lambda_{\max}, m\mu$	$\epsilon$	$\lambda_{\max}, m\mu$	$\epsilon$	$\lambda_{\max}, m\mu$	$\epsilon$
C <sub>6</sub> H <sub>14</sub>	697.5	47	395.0	2000	299.5	8200
CCl <sub>4</sub>	697.5	65	400.0	2600	300.0	10900
Et <sub>2</sub> O	702.5	44	391.0	2650	302.0	8900
C <sub>6</sub> H <sub>6</sub>	697.5	60	402.5	2200	306.0	8700
CHCl <sub>3</sub>	685.0	55	406.0	2250	306.0	10900
EtOH	715.0	53	389.0	3400	304.0	7800
H <sub>2</sub> O	673.0	31	399.0	2300	308.0	6300

presence of small amounts of the oxime tautomer. The electronic spectrum of 5-methoxy-2-nitrosophenol shows evidence for the presence of an intramolecular hydrogen bond as well as for the existence of the oxime tautomer. 5-Dimethylamino-2-nitrosophenol shows clear evidence for the solvent-dependent equilibrium between the phenol and the oxime tautomers. The absorption spectra as well as the polarography of *o*-nitrosophenols and their metal complexes have been reported recently<sup>56</sup>.

Alcoholic solutions of  $\beta$ -,  $\gamma$ - and  $\delta$ -tocopherols form yellow nitroso derivatives on treatment with HNO<sub>2</sub>. The  $\alpha$ -tocopherol does not form the nitroso derivative. The  $\beta$ -,  $\gamma$ - and  $\delta$ -nitrosotocopherols show characteristic absorption at 410, 415 and 405 m $\mu$ , respectively and their mixtures can be analyzed employing these absorption bands<sup>57</sup>.

## B. Nitrosamines

The electronic absorption spectra of several nitrosamines have been reported in the literature<sup>6,7</sup> and the spectra are characterized

by a low intensity absorption maximum around  $360\text{ m}\mu$  which shows fine structure due to the  $n \rightarrow \pi^*$  transition and a relatively intense band around  $235\text{ m}\mu$  due to the  $\pi \rightarrow \pi^*$  transition. The long wavelength band shows solvent blue-shifts characteristic of the  $n \rightarrow \pi^*$  transition (Figure 2). The electronic spectral data of a few nitrosamines are summarized in Table 10. The band due to the  $n \rightarrow \pi^*$  transition around  $360\text{ m}\mu$  is probably characteristic of the

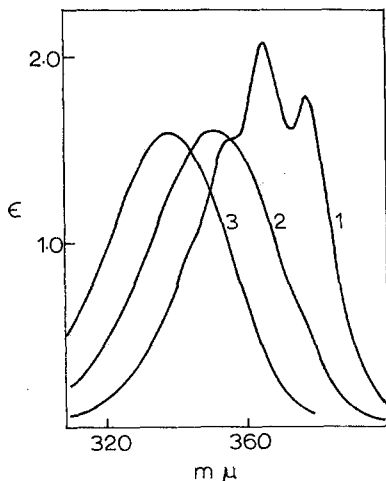


FIGURE 2. Solvent effects on the  $n \rightarrow \pi^*$  band of dimethylnitrosamine: 1, cyclohexane; 2, ethanol; 3, water.

monomeric nitrosamines and dipolar interaction or dimerization markedly affects the position and intensity of this band<sup>7</sup>.

The ultraviolet spectra of several nitrosamines have been reported in recent years: nitrosophenylglycine<sup>58</sup>, nitrosohydroxylamine derivatives<sup>32</sup>, *N*-nitrosoethyleneimine<sup>59</sup>, nitroso derivatives of pyrimidines<sup>60</sup> and other aromatic derivatives<sup>61</sup>. The absence of the characteristic nitroso absorption in the electronic absorption spectrum of methylene diisonitramine has been attributed to internal hydrogen bonding<sup>32</sup>.

Although electronic absorption spectra of nitrosamines have been examined in various solvents including acids<sup>62</sup>, particular mention must be made of the recent studies of Jaffe and coworkers<sup>63,64</sup>, who have examined the basicity of nitrosamines by employing solvent effects on the absorption spectra. The ultraviolet absorption spectra of dialkylnitrosamines in cyclohexane solution containing varying

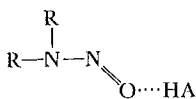
TABLE 10. Electronic absorption spectral data on nitrosamines<sup>6,7</sup>.

Compound	Solvent	$\lambda_{\max}$ , $m\mu^a$			
Dimethylnitrosamine	Light petroleum	374; (105);	361; (125);	351; (98);	232 (5900)
	EtOH	346; (100);	231 (7000)		
Diethylnitrosamine	Light petroleum	378; (90);	366; (105);	233 (6500)	
	EtOH	350; (90)		233 (7400)	
Di- <i>n</i> -propylnitrosamine	Light petroleum	378; (90)	366; (110)	235 (6100)	
	EtOH	350; (90)		233 (7000)	
Di- <i>n</i> -pentylnitrosamine	Light petroleum	378; (90)	366; (105)	356; (85)	236 (6300)
	EtOH	350; (93)			235 (7400)
<i>N</i> -nitrosobis-(2,2,2-trifluoroethylamine)	Light petroleum	386; (91)	372; (113)	360; (86)	230 (5200)
	EtOH	385; (80)	372; (103)		230 (5300)
<i>N</i> -nitrosopiperidine	Light petroleum	377; (65)	365; (70)	238 (4200)	
	EtOH	351; (95)		235 (8100)	
<i>N</i> -nitro- <i>N'</i> -nitrosopiperazine	EtOH	360; (123)	242 (12900)		
Dinitrosopentamethylenetetramine	EtOH	367.5; (115)	230 (10750)		
1,3,5-Trinitroso-1,3,5-triazacyclohexane	EtOH	382; (166)	370; (174)	235 (13200)	

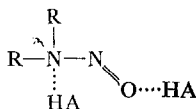
<sup>a</sup> The numbers in parentheses are the extinction coefficients of the absorption bands.

amounts of trichloroacetic acid showed that the intensity of the  $n \rightarrow \pi^*$  band decreased with increase in acid concentration. Further, an isoabsorptive point was found at 346  $m\mu$ . From the analysis of the spectral data it has been shown that the nitrosamine interacts with trichloroacetic acid to form 1:1 hydrogen bonded complexes which in turn react with trichloroacetic acid to form 1:2 complexes. The equilibrium constants of formation of the 1:1 complexes of dialkylnitrosamines vary in the order  $\text{Me} < \text{Et} \cong n\text{-Pr} < i\text{-Pr}$ , while the equilibrium constants of the 1:2 complexes vary in the order  $n\text{-Pr} < \text{Et} \cong i\text{-Pr} < \text{Me}$ . The second hydrogen bond is

supposed to be formed by the lone pair of the amino nitrogen and is likely to be sensitive to steric effects of substituents. The structure of the 1:1 and 1:2 complexes are shown to be **5** and **6**:

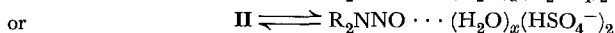
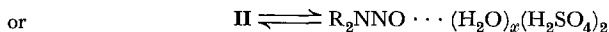
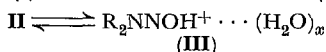
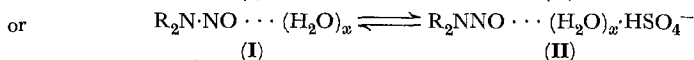
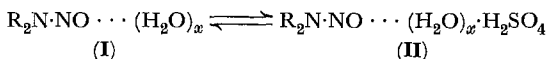


(5)



(6)

Examination of the ultraviolet spectra of dimethyl- and diisopropyl-nitrosamines in solutions of varying concentrations of  $\text{H}_2\text{SO}_4$  has shown that the nitrosamine molecules exist in four spectroscopically distinguishable forms in aqueous acid solutions. The proportion of each form varies with acid concentration. The equilibrium constants of 1:1 and 1:2 hydrogen bonded complexes have been reported for the reactions:



The protonated species does not show the  $n \rightarrow \pi^*$  bands. The  $n \rightarrow \pi^*$  bands of the nitrosamine, however, show decrease in intensity as well as wavelength with increase in acid concentration.

Optically active nitroso compounds have been found to exhibit Cotton effect at the  $n \rightarrow \pi^*$  absorption wavelength<sup>65,66</sup>. Thus, Djerassi and coworkers have found that the C-nitroso group shows Cotton effect at  $\sim 675 \text{ m}\mu$ , while *N*-nitrosamines show the Cotton effect at  $\sim 375 \text{ m}\mu$ . Multiple Cotton effect curves are shown by nitrosamides in the 300–450  $\text{m}\mu$  region. Rotatory dispersion curves of a number of nitroso derivatives of amino acids have been studied and their Cotton effects have been employed for stereochemical assignments.

#### IV. NUCLEAR MAGNETIC RESONANCE SPECTRA

The proton magnetic resonance spectra of a few nitrosamines were examined by Looney and coworkers<sup>67</sup> with a view to study the

hindered rotation about the N—N bond. These workers found that N,N-dimethylnitrosamine gave two signals of equal intensity separated by 19 cps below 180° due to the existence of the *cis* and *trans* isomers. The rate of rotation about the N—N bond was estimated to be 110/sec with a barrier height of  $\sim 23$  kcal. The nuclear magnetic resonance spectrum of *N*-benzyl-*N*-methylnitrosamine showed two isomers below 200° and the integrated intensities of the CH<sub>3</sub> or CH<sub>2</sub> resonances gave a *cis/trans* ratio of 1:3. The temperature dependence of the nmr spectrum indicated that the heat of isomerization was less than 1 Kcal. In *N*-nitroso-*N*-methylaniline as well as *N*-nitroso-*N*-ethylaniline, the presence of only one isomer was indicated in the nmr spectrum. The *cis/trans* ratio in these derivatives was expected to be 20:1, with a very low barrier to rotation.

The proton resonance assignments of Looney and coworkers<sup>67</sup> have been criticized by Brown and Hollis<sup>68</sup> and Karabatsos and Taller<sup>69</sup>, who have assigned the alkyl proton resonances at higher fields to the *cis* isomers rather than to the *trans* isomers. This is because, the nitroso group exhibits anisotropic diamagnetic shielding such that the protons located nearly in line with the double bond are shifted downfield while those located above the double bond are shifted upfield. On the basis of the nmr data, the favored conformations of alkyl nitroso compounds have been assigned by these workers<sup>68,69</sup>. The positions of the proton signals due to *cis* and *trans* isomers of various alkyl nitroso compounds are shown in Table 8. In *N*-methyl-*N*-propylnitrosamine the peak at  $\delta = 3$  has been assigned to the *N*-methyl group *cis* to the nitroso group and the one at  $\delta = 3.8$  to the *trans* *N*-methyl group<sup>68</sup>. *N*-methyl-*N*-phenylnitrosamine predominantly exists with the *cis* methyl and *trans* phenyl configuration.

In alkyl nitrosamines, the trend toward larger values of *trans/cis* ratio in the series Me, Et, *i*-Pr indicates the operation of steric factors. Alkyl nitrites have also been found to behave similar to the nitrosamines, with the *cis*  $\alpha$ -protons appearing at higher fields compared to the *trans*  $\alpha$ -protons<sup>68</sup>. The favored conformations of *trans*-ethyl, *i*-propyl and *t*-butyl groups in the nitroso compounds have been discussed on the basis of the nmr data<sup>69</sup>. In contrast to  $\alpha$ -methyl,  $\alpha$ -methylene and  $\beta$ -methyl protons which resonate at higher fields by about 0.3–0.8 ppm when *cis* to the nitroso oxygen,  $\alpha$ -methine protons resonate at lower fields by about 0.2–0.6 ppm when *cis* (than when *trans*) to the nitroso oxygen. In benzene solvent, the *trans* proton experiences higher upfield shifts than the *cis* proton and this shift-inequality is useful in assigning configurations. The observation of



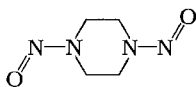
only one set of resonances in the case of *N*-methyl-*N*-phenylnitrosamine is due to the presence of only the *cis* methyl isomer rather than due to rapid interconversion of isomers. In the case of *N*-ethyl-*N*-phenylnitrosamine and *N*-*i*-propyl-*N*-phenylnitrosamine both isomers have been detected by nmr spectra<sup>69</sup>.

TABLE 11. Chemical shifts ( $\tau$  values) of nitrosamines in  $\text{CCl}_4$ <sup>69</sup>.

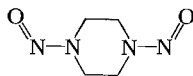
$\text{R}_1\text{R}_2\text{N}\cdot\text{NO}$		$\text{H}\alpha(\text{CH})$		$\text{H}\alpha(\text{CH}_2)$		$\text{H}\alpha(\text{CH}_3)$		$\text{H}\beta(\text{CH}_3)$		Syn/ anti ratio <sup>a</sup>
$\text{R}_1$	$\text{R}_2$	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	
$\text{CH}_3$	$\text{CH}_3$					7.04	6.24			
$\text{CH}_3$	$\text{CH}_2\text{CH}_3$			6.48	5.85	7.07	6.29	8.95	8.62	73/27
$\text{CH}_3$	$\text{CH}(\text{CH}_3)_2$	4.97	5.15			7.13	6.38	8.91	8.58	89/11
$\text{CH}_3$	$\text{C}(\text{CH}_3)_3$					7.11	—		8.46	100/0
$\text{CH}_3$	$(\text{CH}_2)_3\text{CH}_3$			6.53	5.91	7.08	6.30			78/22
$\text{CH}_3$	$\text{CH}_2\text{C}_6\text{H}_5$			5.28	4.70	7.14	6.33			79/21
$\text{CH}_3$	$\text{C}_6\text{H}_5$					6.62				100/0
$\text{CH}_2\text{CH}_3$	$\text{CH}_2\text{C}_6\text{H}_5$			5.28 (6.58)	4.76 (5.93) <sup>b</sup>			9.08	8.67	53/47
$\text{CH}_2\text{C}_6\text{H}_5$	$\text{CH}(\text{CH}_3)_2$	5.13	5.43	5.30	4.75			9.02	8.58	82/18
$\text{CH}_2\text{CH}_3$	$\text{C}_6\text{H}_5$			5.99	5.47			8.85		~97/3
$\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5$			4.84						100/0
$\text{CH}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5$	4.88	4.97					8.82	8.55	64/36
$\text{CH}(\text{CH}_3)_2$	$\text{CH}(\text{CH}_3)_2$	5.11	5.74					8.85	8.48	

<sup>a</sup> Syn refers to the isomer with  $\text{R}_1$  *cis* to the oxygen. <sup>b</sup> Methylene of the ethyl group.

In 1,4-dinitrosopiperazine, the existence of *cis* and *trans* isomers of the type 7 and 8 have been identified in the nmr spectra<sup>70</sup>. The two intense peaks at  $\tau = 5.394$  and 6.175 have been assigned to the



(7)

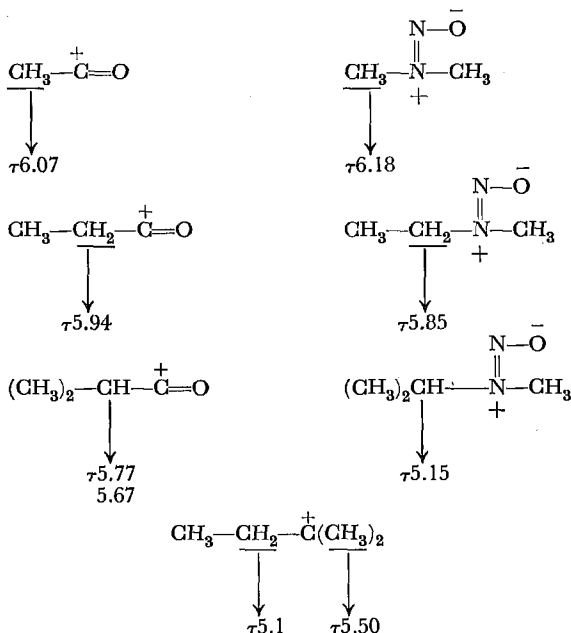


(8)

*cis* isomer, where the four protons of one  $\text{CH}_2\text{CH}_2$  group are equivalent, but differ from those of the other  $\text{CH}_2\text{CH}_2$  group. There is negligible coupling between the protons of the two groups. The low field peak is due to the  $\text{CH}_2\text{CH}_2$  group *trans* to the nitroso group. In the *trans* isomer both the  $\text{CH}_2\text{CH}_2$  groups are equivalent. 1,4-Dinitrosopiperazine is approximately 60% *trans* in acetone. The chemical shift of a particular proton is affected by both the nitroso groups but not equally.

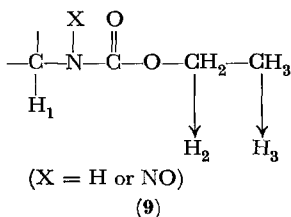
The  $F^{19}$  nmr spectrum of the dimer  $(CF_3)_2NONO$  shows a single sharp fluorine resonance indicating the equivalence of all the fluorine atoms<sup>31</sup>. Apparently, in perfluorinated-*N*-nitritoamine there is no rotational isomerism and there is free rotation about the  $NO-NO$  as well as about the  $N-ONO$  bonds.

The proton chemical shifts in carbonium ions, particularly acyl cations, have been found to be nearly the same as those in *N*-nitrosamines, as can be seen from the data given below<sup>71</sup>:



Since the electron deficient atoms are trigonal in both the species, *N*-nitrosamines may serve as useful models for the nmr study of carbonium ions.

Nmr spectra of *N*-nitrosourethanes have been compared with those of urethanes and the effect of nitrosation on the deshielding of the protons  $H_1$ ,  $H_2$  and  $H_3$  in structure 9



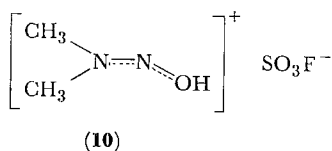
has been studied<sup>72</sup>. Nitrosation deshields all the three protons  $H_1$ ,  $H_2$  and  $H_3$  as shown by the following data:

<i>N</i> -Alkyl group	Deshielding on nitrosation		
	$H_1$	$H_2$	$H_3$
$C_6H_5-CH_2$	0.63	0.47	0.20
$n-C_4H_9$	0.58	0.47	0.26
cyclo- $C_6H_{11}$	1.10	0.40	0.22
$i-C_3H_7$	1.03	0.41	0.24

The absence of restricted rotation about the *N*-carbonyl bond in urethanes as well as in *N*-nitrosourethanes indicates that the changes in chemical shifts accompanying nitrosation are due mainly to the anisotropy of the nitroso group.

The internal rotation of *p*-nitrosodimethylaniline has been studied by the proton spectrum and the heat of isomerization found to be  $\sim 11$  Kcal/mole<sup>73</sup>. The results are in conformity with the  $N=O$  torsional frequency ( $110 - 180\text{ cm}^{-1}$ ) in the far infrared region.

Protonation of *N,N*-dimethylnitrosamine in conc  $H_2SO_4$ , 72%  $HClO_4$ ,  $CF_3COOH$  and  $HFSO_3$  has been examined by the proton magnetic resonance spectrum<sup>74</sup>. Monoprotonation is found to take place only in fluorosulfuric acid around  $0^\circ$ , giving rise to a new signal due to the protonated species **10**. *N,N*-Diethylnitrosamine



and *N*-nitrosopiperidine also show signals due to the protonated species in fluorosulfuric acid.

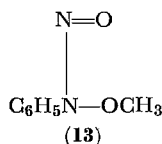
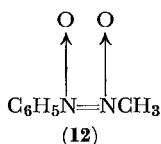
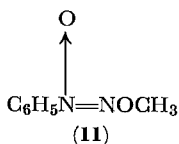
Recently, Freeman<sup>75</sup> has studied the nmr spectra of dimers of C-nitroso compounds and some of the data are summarized below:

$\alpha$ -Nitrosotoluene (dimer)	$CH_2$	4.62
<i>cis</i> -Nitrosomethane (dimer)	$CH_3$	5.80
<i>trans</i> -Nitrosomethane (dimer)	$CH_3$	6.00
<i>t</i> -Nitrosobutane (dimer)	$CH_3$	8.40
<i>t</i> -Nitrosobutane (monomer)	$CH_3$	8.75

The dimer of  $\alpha$ -nitrosotoluene shows only one methylene signal indicating a symmetrical structure. The *cis* and *trans* nitrosomethane dimers also show single signals due to the methyl group. The difference in the chemical shifts of the *cis* and *trans* dimers is due to the

diamagnetic shielding of the NO group. In the *trans* isomers both methyl groups are *cis* to the oxygen and are therefore shielded, while in the *cis* isomer both methyl groups are *trans* to the oxygen and are not shielded. *t*-Nitrosobutane shows two signals whose intensities are temperature dependent and the two signals at  $\tau$  8.75 and 8.40 may be assigned to the monomer and dimer, respectively. The nmr studies clearly establish the diazine dioxide structure for the dimers of C-nitroso compounds.

Freeman<sup>75</sup> has also examined the nmr spectrum of the alkylation product of nitrosohydroxylamine, which can exist in the isomeric **11**, **12**, and **13** forms. On the basis of the nmr spectrum, it was not



possible to decide between structures **11** and **12**, since O-methyl and *N*-methyl protons resonate at nearly the same fields. However, by analogy with the nmr spectrum of the benzylation product of *N*-nitrosobenzylhydroxylamine, the isomer has been shown to exist with the azoxy structure **11** rather than the diimide dioxide structure **12** assigned earlier<sup>33b</sup>.

Nuclear magnetic resonance spectroscopy clearly shows that *p*-nitrosophenol exists predominantly as the benzoquinone monoxime, in agreement with the results from electronic and infrared spectra<sup>23</sup>.

## V. ELECTRON SPIN RESONANCE SPECTRA

The electron spin resonance spectrum of the radical anion of nitrosobenzene has been studied in fair detail. The radical anion has been produced in the electron transfer reaction of aromatic thiolate ions<sup>76</sup>. A 34-line spectrum of the radical anion has been observed with a line-width (between centers of two extreme components) of 28.7 gauss. The coupling constants have been found to be  $a_{\text{N}} = 8.0$ ,  $a_{\text{H}_p} = 3.9$ ,  $a_{\text{H}_o} = 2.9 \pm 0.1$  and  $a_{\text{H}_m} = 1.1 \pm 0.1$  gauss. These workers have also obtained the nitrosobenzene radical anion by the reaction of potassium *t*-butoxide with nitrosobenzene.

Recently, Levy and Myers<sup>77</sup> have produced the nitrosobenzene radical anion by electrolytic reduction in liquid ammonia and obtained a 30-line electron spin resonance spectrum. The values of the various coupling constants given by these workers<sup>77</sup> are:  $a_{\text{N}} = 7.97$ ;

$a_{H_p} = 2.97$ ;  $a_{H_o} = 3.84, 4.14$ ; and  $a_{H_m} = 0.96, 1.14$  gauss. The calculated spectrum shows good agreement with the observed spectrum. The two *ortho* and *meta* coupling constants arise from the effects of the non-linear C—N—O group held rigidly in a planar conformation.

The nitroso compound,  $\text{AcOCH}_2\text{CMe}_2\text{NO}$ , which is colorless as a pure solid, gives rise to a deep blue solution which shows a signal in the electron spin resonance spectrum<sup>78</sup>. A 0.1 M solution of the compound in toluene showed hyperfine splitting with three sharp bands of equal intensity with a g factor of 2. It is suggested that the compound contained 6% of the biradical  $\text{RN}\cdot\text{ON}\cdot\text{OR}$  derived from the dimer of the nitroso compound.

## VI. MICROWAVE SPECTRA

Recently, the rotation spectrum of nitrosobenzene has been studied in the region 13000–24000 Mc/sec by Hanyu and Boggs<sup>79</sup>, employing a Stark-modulated spectrometer with 100 Kc/sec square wave modulation. A spectrum with about 250 lines has been observed, but no quadrupole structure could be resolved. Several *a*-type R-branch transitions have been identified with band centers separated by about 2890 Mc/sec. The rotational constants have been determined. Nitrosobenzene molecule is found to be planar with the CNO group bent at an angle of  $116^\circ$  in the plane of the ring.

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## CHAPTER 4

# The photochemistry of the nitro and nitroso groups

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I. INTRODUCTION . . . . .	166
II. SPECTROSCOPY OF THE NITRO GROUP . . . . .	167
III. PRIMARY PHOTOCHEMICAL PROCESSES OF NITRO COMPOUNDS . . . . .	168
A. A Convenient Representation of the Reactive Excited State(s) . . . . .	168
B. Possible Primary Photochemical Reactions . . . . .	170
C. Dissociation into Free Radicals . . . . .	170
D. Nitrogen-Oxygen Bond Cleavage . . . . .	172
E. Photocycloelimination . . . . .	175
F. Cis-Trans Isomerization . . . . .	175
G. Olefin Photocycloaddition . . . . .	176
H. Nitrite Formation . . . . .	177
I. Hydrogen Abstraction . . . . .	181
1. Evidence for and mechanism of hydrogen abstraction . . . . .	181
2. The <i>o</i> -nitrobenzaldehyde rearrangement and related reactions . . . . .	185
J. Radical Anion Formation . . . . .	191
K. Nitro Photocycloaddition . . . . .	192
IV. Photoinduced Nucleophilic Substitution of Nitroaromatics . . . . .	200
V. Ultraviolet Spectroscopy of Nitroso Compounds . . . . .	202
VI. Primary Photochemical Processes of the Nitroso Group . . . . .	203
A. Compilation of Primary Photochemical Acts . . . . .	203
B. Photodissociation . . . . .	203
1. Nitroxide formation . . . . .	203
2. <i>N</i> -Nitritoamine formation . . . . .	205
3. Mass spectral data . . . . .	206
C. Hydrogen Abstraction . . . . .	206
D. Photocycloelimination . . . . .	207
E. Halogen Atom Expulsion . . . . .	207
VII. ACKNOWLEDGMENTS . . . . .	208
VIII. REFERENCES . . . . .	208
IX. ADDENDA . . . . .	212

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## I. INTRODUCTION

Although the light induced reactions of nitro compounds have been the subject of investigation since the nineteenth century, this area of photochemistry has only recently been exposed to the wealth of techniques now available to the modern investigator. As a result, our knowledge of the photochemistry of nitro compounds is mainly qualitative with relatively little available in the way of quantum yield data and kinetic studies. Likewise, emission spectroscopy, a powerful tool for elucidating the nature of lowest excited states, has been employed only sparingly on the substrates to be discussed.

This state of affairs contrasts sharply with the present status of the carbonyl functional group, the photochemistry of which has been extensively studied by physical and organic chemists and is, in many cases, fairly well understood. The photochemistry of aldehydes and ketones has been safely categorized into a number of primary photochemical processes<sup>1,2</sup>, an understanding of which has led to the prediction of new reactions and allowed for the explanation of others. By contrast, the large number of known photochemical reactions of nitro compounds has commonly been treated as a group of separate entities; only recently have attempts been made to classify them in some fashion. De Mayo<sup>3</sup> rationalized a number of photorearrangements of aromatic nitro compounds by postulating preliminary hydrogen abstraction as a common primary act. More recently, Calvert and Pitts<sup>2</sup> tabulated several primary processes for nitro compounds but these can account for but a small fraction of the known photochemistry in this area.

It is with this in mind that I have ventured herein to categorize essentially all of the known photochemical reactions of nitro (and nitroso) compounds with the use of expanded lists of primary processes. *Inevitably, some of these primary acts are mere postulates with only the faintest of experimental support; the listing of a given reaction with a particular primary act may be due entirely to mechanistic reasoning.* My justifications for compiling the chapter in this fashion are (1) the hope that the postulates made here will encourage the experimentation necessary to verify or alter them and (2) that by providing the large body of data in this fashion, it will become clear that a number of the sometimes extraordinary rearrangements rest on common ground.

No attempt has been made in this chapter to provide a review of the general theories and vocabulary of photochemistry. The reader

who is new to this area is referred to the excellent texts<sup>2,4</sup> now available for an explanation of the basic concepts and nomenclature used herein.

## II. SPECTROSCOPY OF THE NITRO GROUP

Since chapters one and two of this monograph deal with the theory and spectroscopy of the nitro group, the discussion in this section will be limited to a review of those data most appropriate to a rationalization of the photochemistry.

Until recently, the ultraviolet absorption spectra of nitroalkanes were considered unexceptional, there being typically two bands observed. One of these appears at ca. 270  $m\mu$  with low intensity and is assigned to an  $n \rightarrow \pi^*$  transition; the other band is observed at ca. 200  $m\mu$  with  $\epsilon \cong 5000$  and is considered to be due to a  $\pi \rightarrow \pi^*$  transition.<sup>5-7</sup> However, the situation is now beclouded by the observation<sup>8,9</sup> of a third, as yet unexplained, transition at ca. 350  $m\mu$  in the absorption and circular dichroism spectra of several nitro steroids. In the absence of a definitive assignment for this band we will continue to assume that the lowest lying singlet and triplet states of nitroalkanes are  $n$ ,  $\pi^*$ , an assumption which is supported by emission data for nitroaromatics (see below). The possibility has been raised<sup>9</sup> that this band is due to a second  $n \rightarrow \pi^*$  transition, though it was felt that this was unlikely (cf. Chapter 2 Figure 9).

The present state of affairs is equally confused for nitroolefins. The ultraviolet absorption spectrum of 1-nitro-1-propene is reported<sup>10</sup> to contain bands at 229  $m\mu$  ( $\epsilon = 9400$ ) and 235  $m\mu$  ( $\epsilon = 9700$ ) assigned as charge-transfer transitions.<sup>11</sup> Though no sign of the expected, displaced  $n \rightarrow \pi^*$  transition could be observed, recent studies<sup>12</sup> with nitroethylene have revealed the presence of a long-wavelength band at 305  $m\mu$ . Furthermore, Djerassi and coworkers have also found<sup>8</sup> long-wavelength absorption (350  $m\mu$ ) in the ultraviolet spectrum of 6-nitro- $\Delta^5$ -androstene-3 $\beta$ ,17 $\beta$ -diol and *two* maxima in the circular dichroism spectrum (317 and 395  $m\mu$ ). A circular dichroism study<sup>9</sup> of 6-nitro-cholest-5-ene has likewise revealed two long-wavelength bands (337 and 410  $m\mu$ ) in addition to a presumed charge-transfer transition at 262  $m\mu$ . The higher energy, long-wavelength maximum has been assigned<sup>9</sup> as the  $n \rightarrow \pi^*$  transition but the 400  $m\mu$  band remains anomalous and may be analogous to the 350  $m\mu$  band in the saturated steroids.

Even the spectrum of nitrobenzene is not free from controversy, there being present a long-wavelength absorption maximum at  $330\text{ m}\mu$  which has been assigned<sup>13-16</sup> both as  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$ . However, in one of the few emission studies reported for nitro compounds, Kasha<sup>17</sup> has found that 4-nitrobiphenyl, 2-nitrofluorene and 1,5-dinitronaphthalene all show unique phosphorescence with lifetimes and fine structure indicative of an  $n, \pi^*$  lowest lying triplet state. These data lend strong support to the proposition that nitroaromatics have  $n, \pi^*$  lowest lying singlet and triplet states (and that the nitrobenzene absorption at  $330\text{ m}\mu$  is due to an  $n \rightarrow \pi^*$  transition).

### III. PRIMARY PHOTOCHEMICAL PROCESSES OF NITRO COMPOUNDS

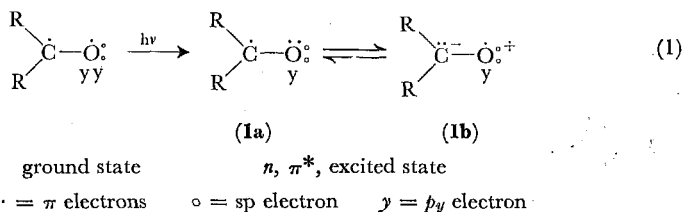
#### A. A Convenient Representation of the Reactive Excited State(s)

In considering the nature of the reactive species in a photochemical process, it is commonly assumed that one need only be concerned with the lowest lying singlet and triplet excited states of the substrate. This postulate is based upon the observation that molecules ordinarily fluoresce and phosphoresce from their lowest singlet and triplet states respectively; thus, radiationless decay within the singlet and triplet manifolds is too rapid to allow for competition by emission from a higher excited state. The corollary has been that a photochemical process must also originate from one of these lowest levels, and though exceptions have begun to appear in the literature<sup>18,19</sup>, the assumption is still a valuable one for organic photochemistry.

In almost all the studies to be described below, there are insufficient data available to allow for the assignment of multiplicity to the reactive species. However, one can say with some degree of certainty that the  $n, \pi^*$  singlet and triplet states are lowest lying in aliphatic nitro compounds; the evidence, though still somewhat ambiguous, supports a similar conclusion in aromatic and vinyl reactants (cf. section II). It must be recognized that in the latter two cases, the assignment is made even more hazardous by the possibility of inversion of the order of close lying (e.g.  $n, \pi^*$ ;  $\pi, \pi^*$ ) excited states through solvent effects or subtle structural changes. However, in the absence of more definitive data, *we will assume here that the reactive species in the photochemistry of nitro compounds is an  $n, \pi^*$  excited*

state. The utility of this assumption is that it makes more facile the rationalization of the primary acts to be described below; note, however, that the reality of their existence is by no means dependent on our concept of the reacting excited state.

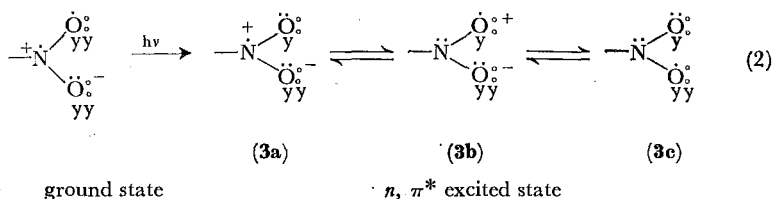
Zimmerman<sup>20</sup> has suggested the representation of an  $n \rightarrow \pi^*$  transition for the carbonyl group shown in reaction 1. Structure (**1a**)



suggests that the  $n, \pi^*$  excited state has considerable diradical character since the isolated electron on oxygen is orthogonal to the  $\pi$  system. With reference to hydrogen abstraction, the excited state has been found to resemble an alkoxy radical. A shorthand replacement for structures **1a** and **1b** is the simplified form **2**. Using this

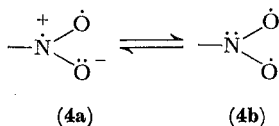


nomenclature, the  $n \rightarrow \pi^*$  transition of the nitro group may be pictured as shown in reaction 2. Two provocative conclusions are



suggested by the mesomeric forms **3a-c**. First, the photochemistry of nitro compounds should have much in common with that of carbonyl compounds since structures **1a** and **3a** are both diradicals. This appears to be borne out by the facts (cf. Table 1, section III.B). Secondly, the resonance structure **3c** implies that a nitro  $n, \pi^*$  excited

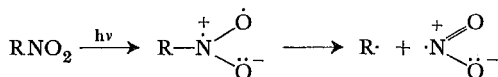
state may also be found to exhibit 1, 3 diradical properties. Again, a shorthand notation is shown in structures **4a** and **4b**.



### B. Possible Primary Photochemical Reactions

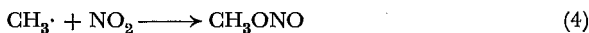
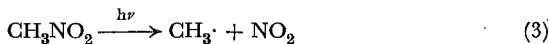
The primary acts which are considered in this review are listed in Table 1. Where there is sufficient analogy to the known photochemistry of ketones and aldehydes, a comparable reaction in that series is also listed<sup>1,2</sup>.

### C. Dissociation into Free Radicals



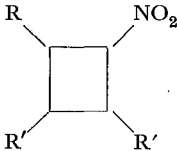
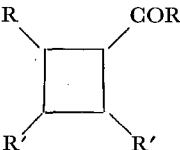
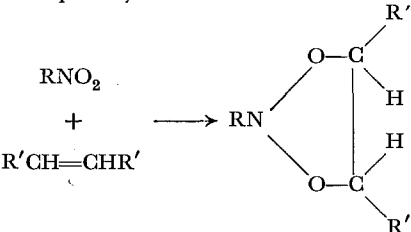
The evidence for cleavage of the carbon-nitrogen bond as a primary act derives mainly from studies with nitroaliphatics, particularly nitromethane. It is known that the pyrolysis of these molecules results in cleavage of this bond, the dissociation energy of which is ca. 57 kcal/mole<sup>21</sup>. This value is well below the 95 kcal/einstein associated with 3130 Å light.

The first proposal<sup>22</sup> that photodissociation was the initial reaction produced by irradiation of gaseous nitromethane was made in 1955 as a means of rationalizing data then in the literature<sup>23</sup>. It had previously been felt that nitromethane first rearranged to methyl nitrite (a product later isolated) *via* an intramolecular rearrangement and that the nitrite subsequently underwent further decomposition. However, methyl nitrite formation could also be explained by a primary dissociative step followed by recombination (reactions 3 and 4).

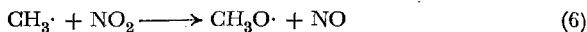
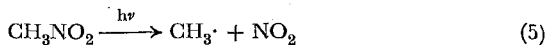


The observation of methane as a photoproduct (presumably due to hydrogen abstraction by the methyl radical) has been taken<sup>24</sup> as evidence for primary photodissociation. Rearrangement cannot, in any case, be the *sole* source of methyl nitrite, since Rebbert and

TABLE 1. Primary photochemical processes of nitro compounds.

Nitro compounds	Carbonyl compounds
1. Dissociation into free radicals $\text{RNO}_2 \longrightarrow \text{R}\cdot + \text{NO}_2$	$\text{RCOR} \longrightarrow \text{R}\dot{\text{C}}\text{O} + \text{R}\cdot$
2. Nitrogen-oxygen bond cleavage. $\text{RNO}_2 \longrightarrow \text{R}\dot{\text{N}}\text{O} + \text{O}$	
3. Photocycloelimination $\text{RCH}_2\text{CH}_2\text{NO}_2 \longrightarrow \text{RCH}=\text{CH}_2 + \text{HNO}_2$	$\text{RCOCH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{RCO}\dot{\text{C}}\text{H}_3 + \text{CH}_2=\text{CH}_2$
4. <i>Cis-trans</i> photoisomerization $\text{cis-RCH}=\text{CHNO}_2 \rightleftharpoons \text{trans-RCH}=\text{CHNO}_2$	$\text{cis-RCH}=\text{CHCOR} \rightleftharpoons \text{trans-RCH}=\text{CHCOR}$
5. Olefin photocycloaddition $\text{RCH}=\text{CHNO}_2$ $+ \text{R}'\text{CH}=\text{CHR}' \longrightarrow$ 	$\text{RCH}=\text{CHCOR}$ $+ \text{R}'\text{CH}=\text{CHR}' \longrightarrow$ 
6. Nitrite formation $\text{RNO}_2 \longrightarrow \text{RONO}$	
7. Hydrogen abstraction $\text{RNO}_2 + \text{R}'\text{H} \longrightarrow \text{R}\dot{\text{N}}\text{O}_2\text{H} + \text{R}'\cdot$	$\text{RCOR} + \text{R}'\text{H} \longrightarrow \text{R}\dot{\text{C}}(\text{OH})\text{R} + \text{R}'\cdot$
8. Radical anion formation $\text{RNO}_2 + e^- \longrightarrow \text{RNO}_2^{\cdot-}$	
9. Nitro photocycloaddition $\text{RNO}_2 + \text{R}'\text{CH}=\text{CHR}' \longrightarrow$ 	

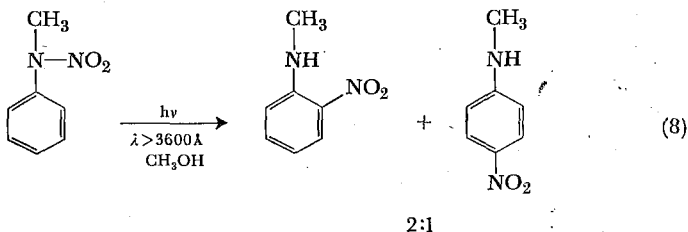
Slagg found<sup>25</sup> that introduction of  $N^{15}O$  into the photolysis results in the formation of  $CH_3ON^{15}O$ . Reactions 5-7 have been proposed to explain this observation.



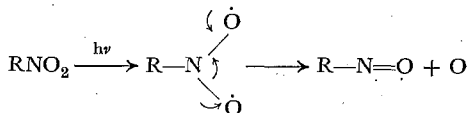
More conclusively, the esr spectrum of  $NO_2$  has been recorded during the photolysis of nitromethane, nitroethane and nitropropane<sup>26</sup>. This is the first direct evidence for the formation of  $NO_2$ . Of interest is the fact that the quantum yield for methyl nitrite formation is higher at 2537 Å than at 3130 Å<sup>25</sup>. Methyl nitrite has been observed as a photolysis product in an argon matrix<sup>27</sup> at 20°K as well as in the liquid and gas phases.

Although there is substantial evidence for photodissociation as a primary act, the available evidence does not exclude the possibility of concomitant intramolecular rearrangement to methyl nitrite<sup>28</sup>—further discussion of this reaction is reserved for section III.H. It has been suggested<sup>29</sup> that nitrobenzene may dissociate into phenyl radical and nitrogen dioxide but no substantial evidence for this process has appeared. An alternative primary act (N—O bond cleavage) has been proposed<sup>30</sup> (cf. section III.D).

The photolysis of an *N*-nitro aromatic<sup>31</sup>, which appears to result in dissociation, is shown in reaction 8.

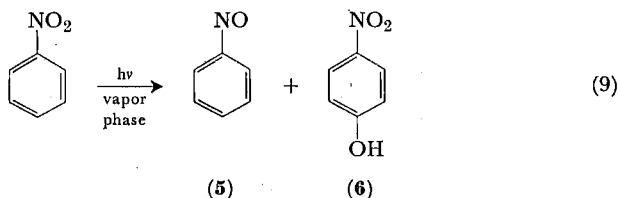


#### D. Nitrogen-Oxygen Bond Cleavage

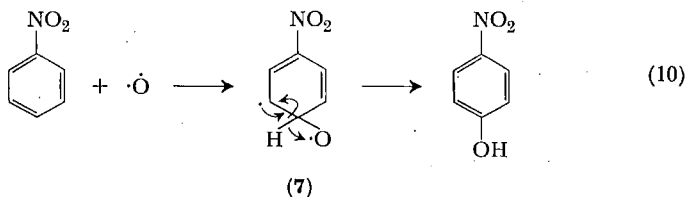


It is now well recognized<sup>32,33</sup> that nitrogen dioxide efficiently ( $\phi = 0.97$ ) dissociates into nitric oxide and atomic oxygen upon

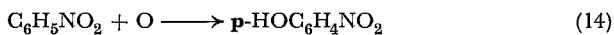
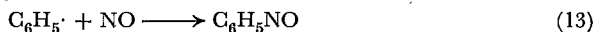
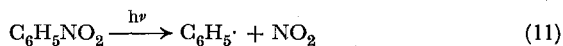
irradiation with 3130 and 3160 Å light (the dissociation energy has been given<sup>33</sup> as 71–72 kcal/mole). An analogous process has been suggested for nitrobenzene to rationalize the products isolated upon its photolysis in the vapor phase (reaction 9)<sup>30</sup>. Fission of the nitrogen–



oxygen bond would lead directly to nitrosobenzene and atomic oxygen; the latter could conceivably oxidize nitrobenzene to the phenol (reaction 10)<sup>30</sup>.



Several other mechanisms are feasible, however, and require consideration. One is dissociation to phenyl radical and nitrogen dioxide (section III.C) followed by photolysis of the nitrogen dioxide to produce nitric oxide and atomic oxygen. Further reaction would give the observed products (reactions 11–14).



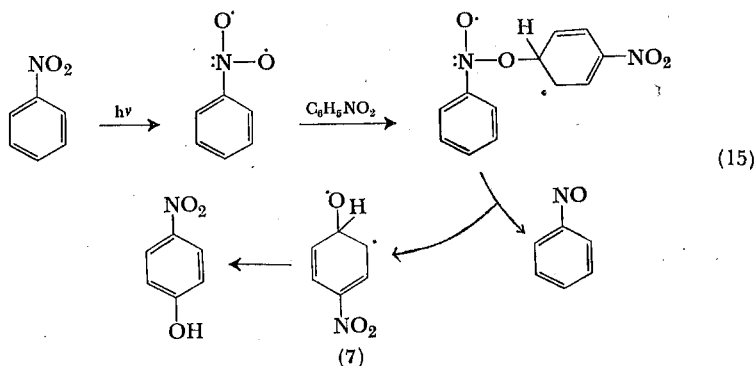
(7)

As regards reaction 12, it is interesting that only recently have investigators been able to find nitrogen dioxide among the photolysis products of nitromethane, even though the formation of this molecule occurs in the primary act (cf. section III.C).

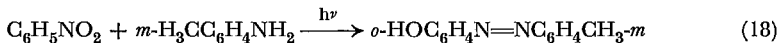
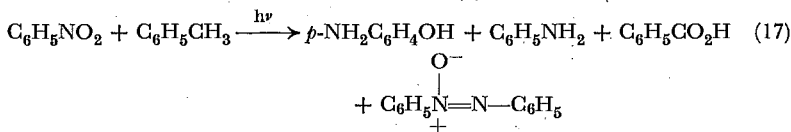
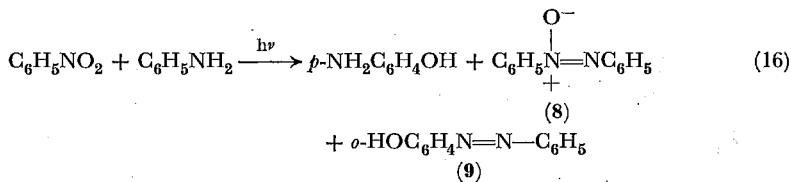
A second possible rationale for reaction 9 would be photoaddition of excited nitrobenzene to a ground state molecule; cleavage to nitrosobenzene and the diradical (7) would then account for the



products (reaction 15). Analogous reactions are discussed in section III.K.



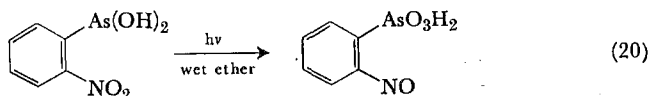
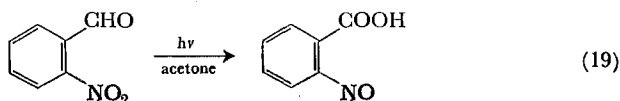
In support of their proposal for nitrogen-oxygen bond cleavage in nitrobenzene, Hastings and Matsen cite<sup>30</sup> the liquid phase studies of Vecchiotti and his coworkers<sup>34-36</sup> (reactions 16-18).



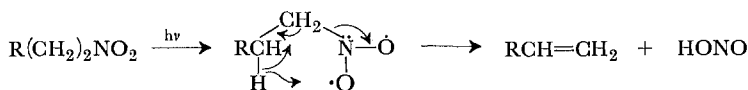
However, in the light of recent studies on the photoreduction of nitrobenzene by hydrogen donors (cf. section III.I), there is a good possibility that hydrogen abstraction and not oxygen atom formation is the primary act responsible for these reactions. The products are readily explained if one assumes that nitrosobenzene and phenylhydroxylamine are the initial products. Phenylhydroxylamine is known to rearrange to *p*-aminophenol; nitrosobenzene and phenylhydroxylamine rapidly condense to give azoxybenzene (8) which, in turn, is known to rearrange to *o*-hydroxyazobenzene (9). In fact, nitrobenzene is reported<sup>37</sup> to be stable to 3660 Å light when dissolved in benzene, a solvent which is a poor hydrogen donor.

Conversion of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid (reaction 19) has been cited<sup>38</sup> as another reaction which may be a consequence of N-O bond cleavage; the initial act here may also

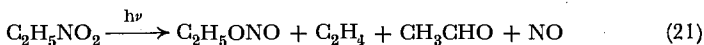
be hydrogen abstraction and is discussed in detail in section III.I. A more unusual example<sup>39</sup> of intramolecular oxidation-reduction is reaction 20.



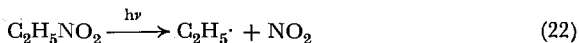
### E. Photocycloelimination



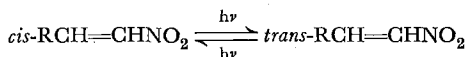
This primary process, reminiscent of the Type II process of carbonyl photochemistry, has been suggested<sup>25</sup> to account for the formation of ethylene during the gas and liquid phase photolyses of nitroethane (reaction 21).



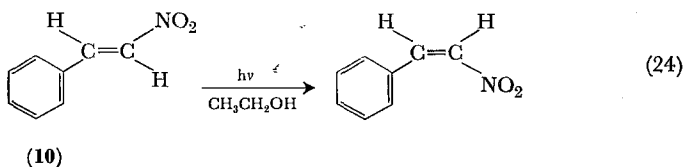
Paszyc has proposed<sup>28</sup> that the ethylene is formed, not through such unimolecular decomposition, but by the disproportionation of two ethyl radicals originating from photodissociation (reactions 22 and 23).



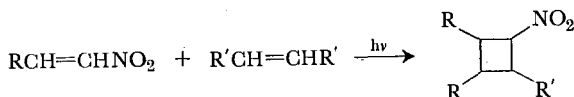
### F. Cis-trans Photoisomerization



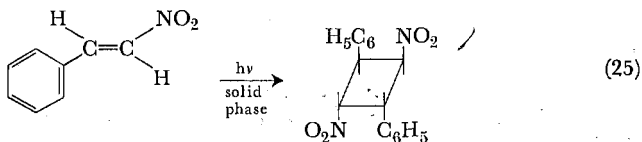
In 1957, Miller reported<sup>40</sup> that *trans*- $\beta$ -nitrostyrene (**10**) could be photolytically isomerized to the *cis* isomer (reaction 24). More recently, several other examples of *cis-trans* isomerization of nitrostyrenes have been published<sup>41</sup>.



### G. Olefin Photocycloaddition

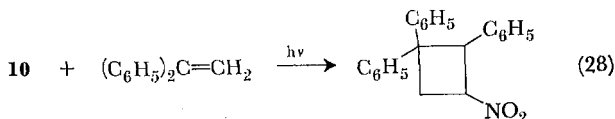
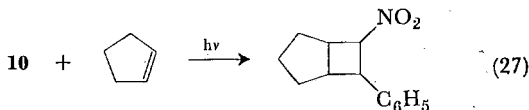
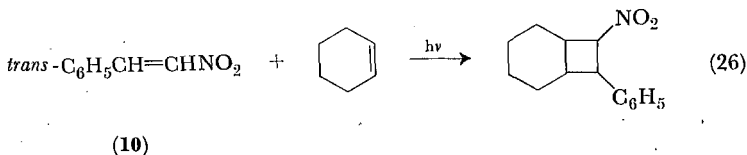


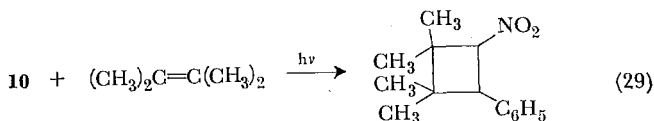
Although a photodimer of *trans*- $\beta$ -nitrostyrene was first isolated<sup>42</sup> in 1884, it wasn't until recently that its structure was established<sup>40,43</sup> (reaction 25). The dimerization occurs only in the solid phase;



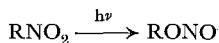
irradiation of a solution of *trans*- $\beta$ -nitrostyrene affords only the *cis* isomer as the product (section III.F). The resistance of the *cis* isomer towards dimerization may be related to the recent observation<sup>41</sup> of photochromism in *cis*- $\beta$ -nitrostyrenes (cf. section III.K).

Cycloaddition of  $\beta$ -nitrostyrene with a variety of olefins has been reported by Chapman and coworkers<sup>44</sup> (reactions 26–29). In all cases, the phenyl and nitro groups are found to be *trans* to one another in the product<sup>45</sup>. The absence of products with *cis* stereochemistry may again be related to preferential photochromism of *cis*- $\beta$ -nitrostyrenes (see above).

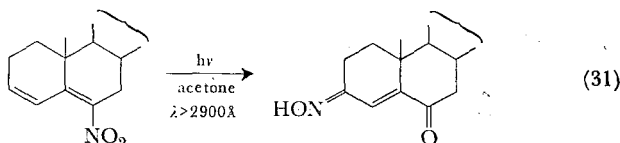
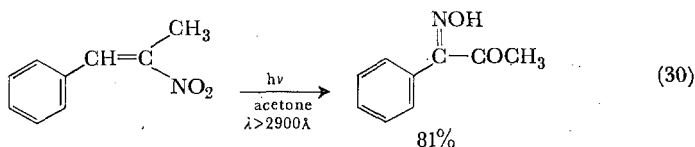




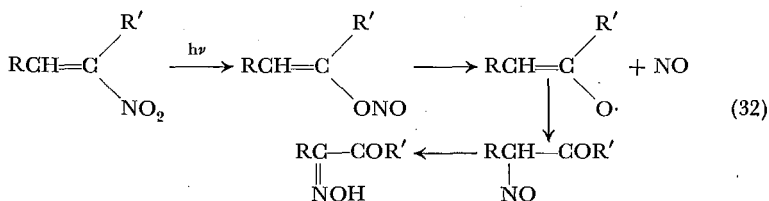
## H. Nitrite Formation



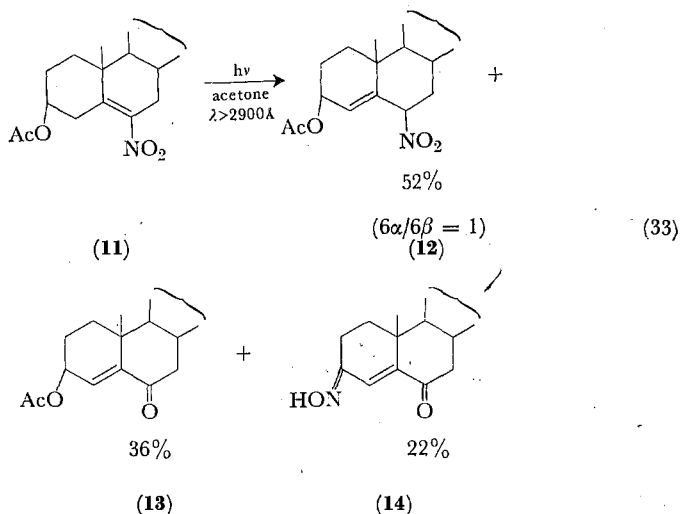
Until recently, this process was favored as the primary photochemical act of nitroalkanes (section III.C); although this is no longer felt to be so, nitrite formation has recently been resurrected as a means of rationalizing the photo-induced rearrangement of  $\alpha,\beta$ -unsaturated nitro compounds to  $\alpha$ -oximinoketones (reactions 30 and 31)<sup>44,46</sup>. The mechanism suggested for these rearrangements is



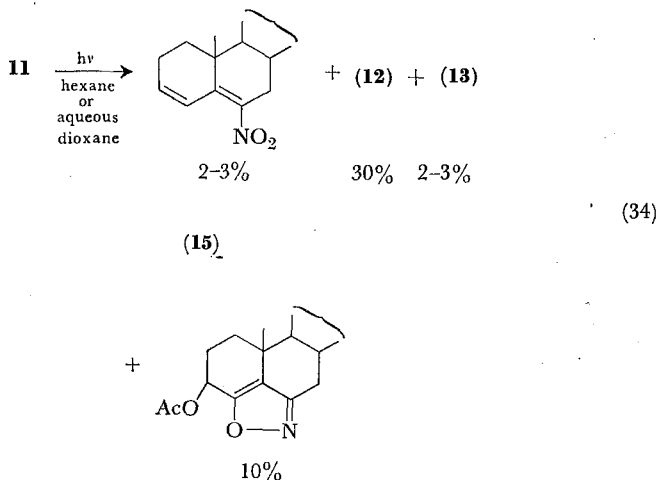
shown in reaction 32. Although acetone is not essential for the reaction, its use as solvent does lead to the highest yield of product and it may therefore be serving as a sensitizer.



An apparently related reaction<sup>46</sup> is the rearrangement of 6-nitro- $\Delta^5$ -cholesteryl-3 $\beta$ -acetate (**11**). The oximinoketone (**14**) is

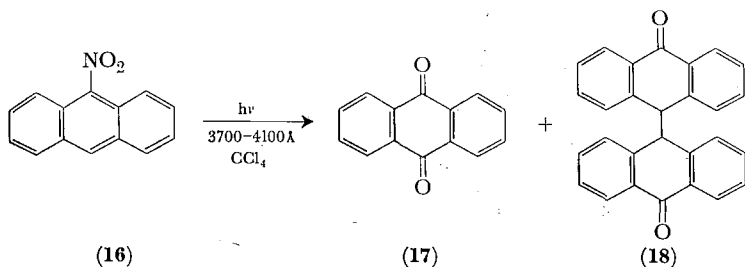


regarded as having been formed from 6-nitrocholesta-3,5-diene (**15**) (cf. reaction 32), a compound which can indeed be isolated when the irradiation of **11** is conducted in hexane or aqueous dioxane (reaction 34)<sup>47</sup>.

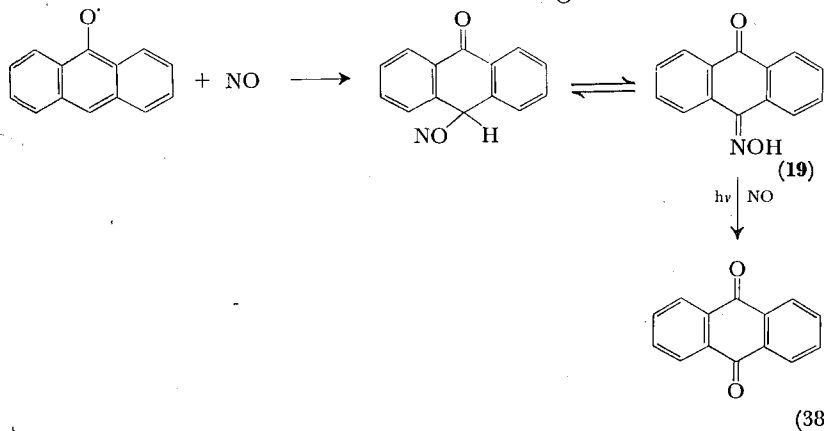
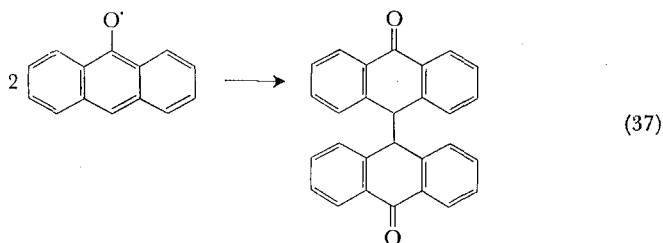
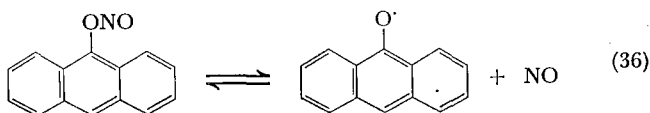
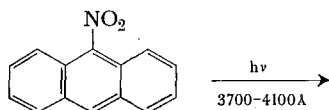


Initial rearrangement to a nitrite has also been postulated to explain the formation of anthraquinone (**17**) and 10,10'-bianthrone

(18) upon photolysis of 9-nitroanthracene (16)<sup>48-51</sup>. The proposed<sup>48</sup>

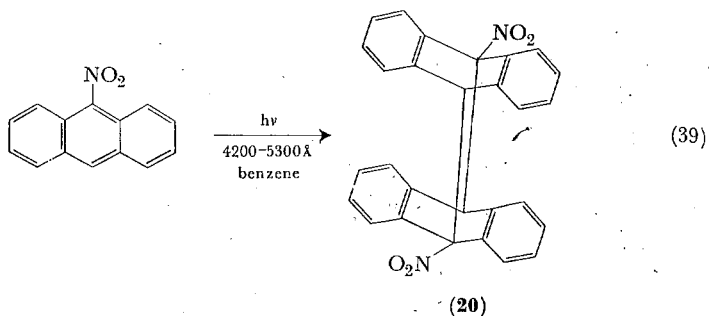


mechanism is shown in reactions 36-38. Anthraquinone monoxime



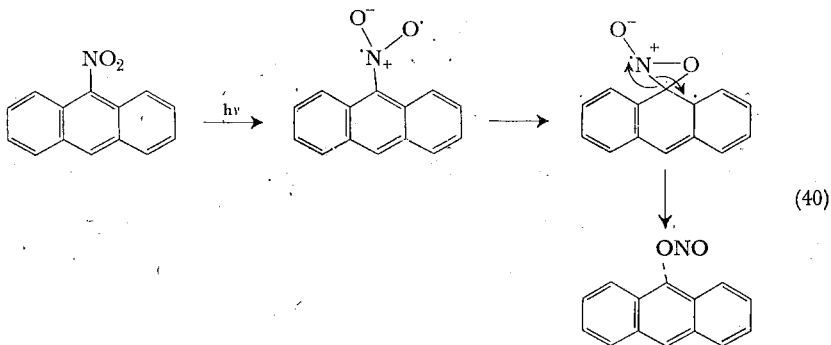
(19) has, in fact, been isolated from these photolyses and been shown to convert to anthraquinone upon irradiation in the presence of nitric oxide. If the nitric oxide produced in reaction 36 is efficiently swept from the system, reaction 38 is inhibited and the bianthrone (18) can be isolated in yields as high as 86 %.

It is interesting to note that irradiation<sup>51</sup> of 9-nitroanthracene with longer wavelength light leads not to 17 or 18 but to a dimer, 20, (reaction 39). The difference between reactions 35 and 39 may be



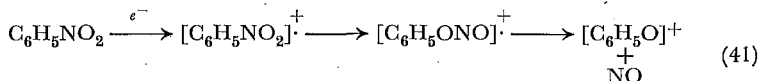
due to the cleavage of 20 when shorter wavelength light is used. Alternatively, Yang has suggested<sup>52,53</sup> that two different excited states are involved in these reactions, with 20 arising from a lower  $\pi, \pi^*$  triplet and 18 being formed *via* an upper  $n, \pi^*$  triplet. Since no fluorescence can be observed in the emission spectrum of 9-nitroanthracene, intersystem crossing is presumed to be highly efficient<sup>54</sup>.

The postulated<sup>48</sup> sequence of events leading to nitrite formation is shown in reaction 40. In reality, the primary act proposed here is the addition of the excited nitro group to a  $\pi$  system; intermolecular versions of such additions are suggested in section III.D (reaction 15) and section III.K. Schemes similar to reaction 40 may be written



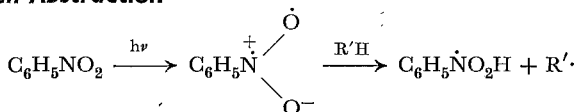
to rationalize the formation of nitrite from nitroolefins (reaction 32) Chapman suggests<sup>48</sup> that the nitro group must be forced from the plane of the  $\pi$  system in order for nitrite formation to occur. Thus nitrobenzene appears to be stable under conditions which bring about the conversion of 9-nitroanthracene to the bianthrone. Nitroaliphatics should not be able to rearrange to nitrite esters if reaction 40 is the requisite mechanism and, indeed, no such rearrangement in this series has yet been substantiated.

The mass spectra of aromatic nitrocompounds<sup>55-57</sup> lend strong support to the overall picture presented here. All show a strong M-30 peak corresponding to the loss of nitric oxide, which in turn, is thought to arise *via* initial rearrangement of the nitro group (reaction 41).



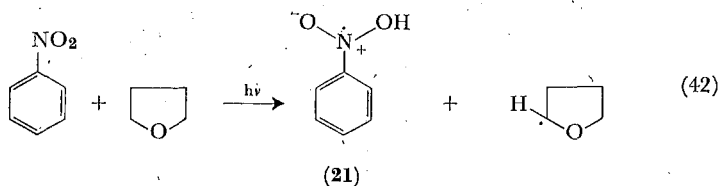
There is no evidence that aliphatic nitrocompounds can rearrange upon electron impact in a similar fashion<sup>58</sup>.

### I. Hydrogen Abstraction



### I. Evidence for and mechanism of hydrogen abstraction

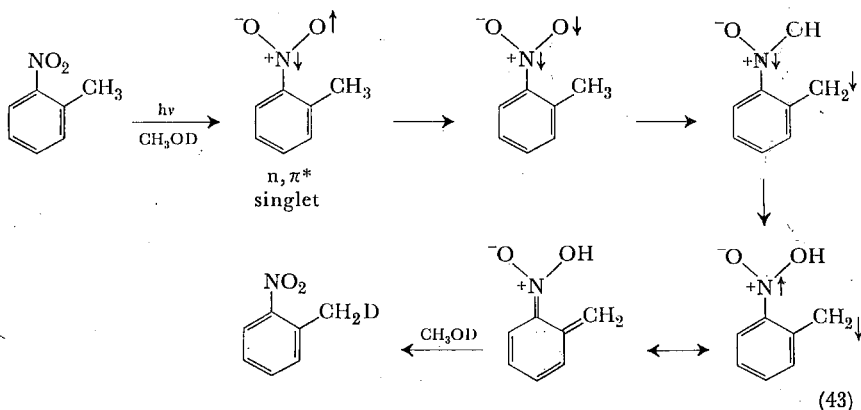
Mention has already been made of the fact that hydrogen abstraction appears to be characteristic of molecules with low-lying  $n$ ,  $\pi^*$  excited states (cf. section II); carbonyl compounds remain the most thoroughly investigated examples. Although the formation of *aci*-nitro structures had been proposed earlier<sup>59-61</sup>, hydrogen abstraction by the photoexcited nitro group was first invoked by de Mayo<sup>62</sup> in 1960 as a general mechanistic approach to nitrophotocchemistry. Substantial evidence for the existence of such a reaction came from the assignment<sup>63</sup> of **21** as the species responsible for the esr spectrum of an irradiated tetrahydrofuran solution of nitrobenzene. An



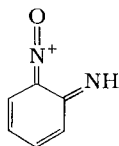


alternative explanation<sup>64</sup> for a similar system had attributed the signal to the formation of the radical anion which would result from electron transfer from the solvent (cf. section III.J); recent data<sup>65</sup> support the interpretation depicted in reaction 42.

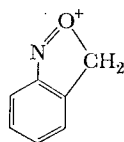
In 1962, Wettermark<sup>66</sup> was able to show that *o*-nitrotoluene was photochromic, a phenomenon presumably caused by the transient formation of a quinoid *aci*-nitro compound. One would predict on this basis that irradiation of *o*-nitrotoluene in a deuterated solvent should result in uptake of deuterium and this has been found to be the case<sup>67</sup>. The full sequence is shown in reaction 43 and incorporates two spin inversion steps because recent evidence implicates the triplet state as the species responsible for hydrogen abstraction (see below).



Initial hydrogen abstraction followed by the loss of HO· is presumably responsible for a M-17 ion as the base peak in the mass spectra of *o*-nitroaniline<sup>68</sup> and *o*-nitrotoluene<sup>69</sup>. Ions **22** and **23** have been suggested as the products of such decomposition.



(22)

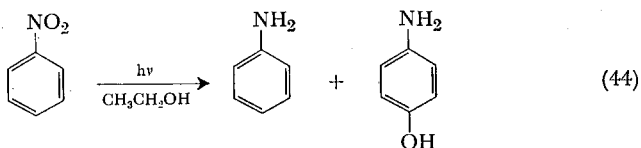


(23)

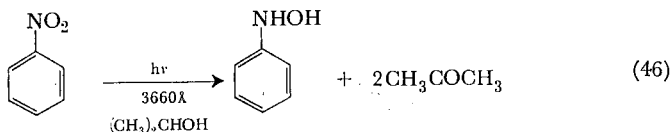
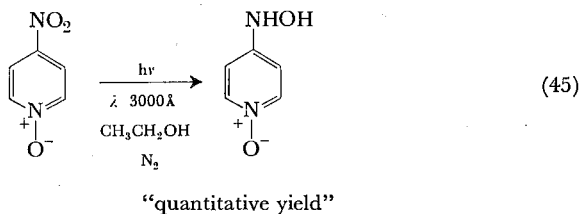
By using perfluoronaphthalene ( $E_{\text{triplet}} = 56.6$  kcal) as a triplet quencher, it has recently been shown<sup>70</sup> that photolytic hydrogen abstraction proceeds via the triplet state of nitrobenzene ( $E_{\text{triplet}} = 60$  kcal). Specific irradiation of nitrobenzene in tetrahydrofuran

containing the quencher gave none of the esr signal associated with  $\text{C}_6\text{H}_5\text{NO}_2\text{H}$ , but a signal attributed to triplet perfluoronaphthalene could be detected at low temperature. It is, of course, still possible that the singlet state is involved in *intramolecular* reactions.

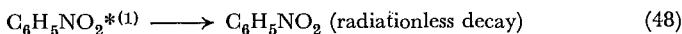
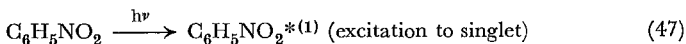
The ultimate product of the photoreduction of nitrobenzene by hydrogen donors appears to be phenylhydroxylamine. Evidence to this effect dates back to the original studies by Ciamician and Silber<sup>71</sup> on the light-catalyzed reaction of nitrobenzene with ethanol (reaction 44). It was assumed that the *p*-aminophenol formed *via* rearrangement of phenylhydroxylamine. The photolytic reduction

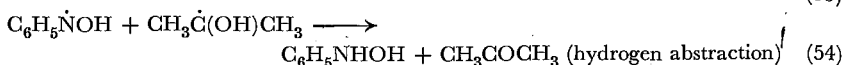
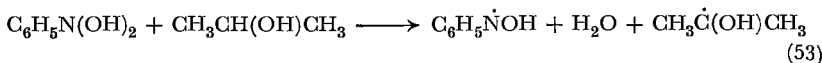
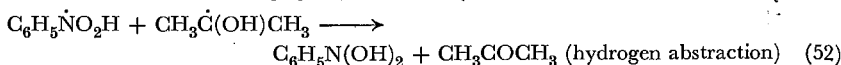
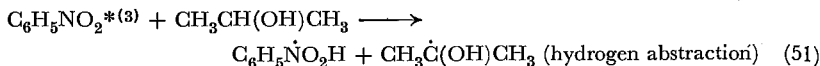
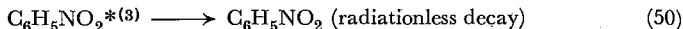
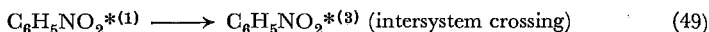


of the nitro group to an hydroxylamino function has recently been conclusively demonstrated with two different substrates<sup>72,73</sup> (reactions 45, 46).

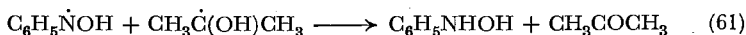
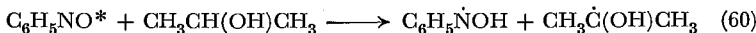
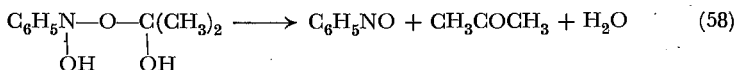
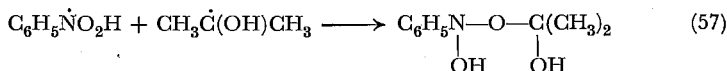
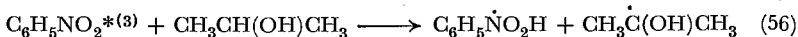


The quantum yield for disappearance of nitrobenzene was found to be  $1.14 \pm 0.1 \times 10^{-2}$ ; the phenylhydroxylamine was identified by its ultraviolet absorption spectrum and by its conversion to nitrosobenzene (also identified by its absorption spectrum)<sup>73</sup>. The suggested<sup>73</sup> mechanism is shown in reactions 47–54.

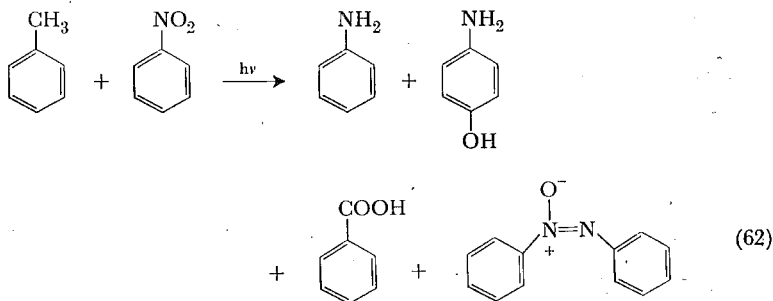




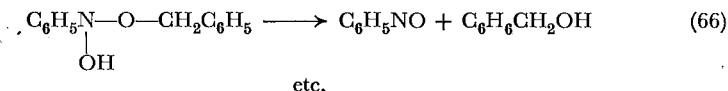
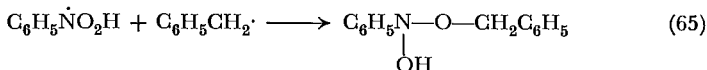
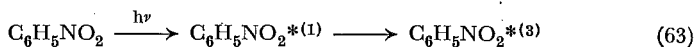
There are several alternative mechanisms which one can write for the formation of phenylhydroxylamine; the most attractive is presented in reactions 55–61.



Reactions 55–58 provide a possible rationale for the known capability of nitrobenzene to photooxidize hydrogen donors. For example, exposure of nitrobenzene and toluene to sunlight leads to the formation of benzoic acid among other products<sup>35</sup> (reaction 62)



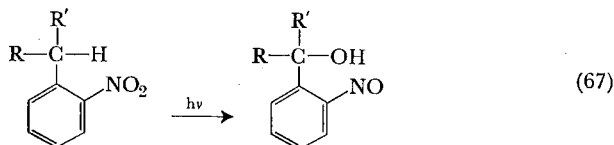
(cf. section III.D). A possible mechanism is presented in reactions 63–66.



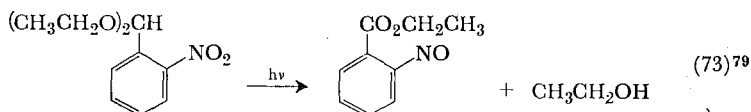
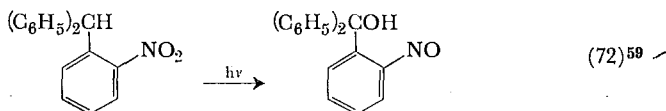
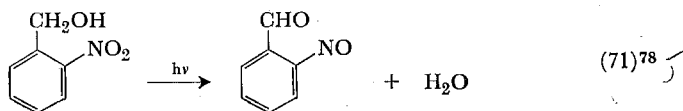
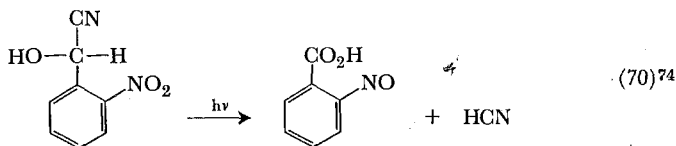
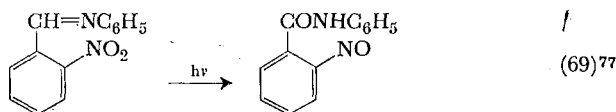
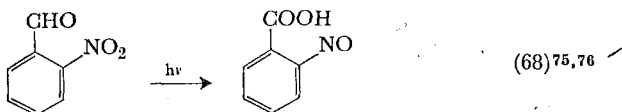
As regards reactions 59–61 the photoreduction of nitrosobenzene is known and will be discussed further in section V. Were  $\text{C}_6\text{H}_5\text{N}(\text{OH})_2$  an intermediate (reaction 52), it would seem more likely that it dehydrate to nitrosobenzene than disproportionate as shown in reaction 53. The two mechanisms given here are readily distinguishable since the acetone formed in reaction 54 retains the isopropyl alcohol oxygen, whereas the carbonyl oxygen formed in reaction 61 is derived from the nitro group.

## 2. The o-nitrobenzaldehyde rearrangement and related reactions

A number of light catalyzed intramolecular rearrangements of nitroaromatics are now known in which the nitro group is reduced to a nitroso function while an oxygen atom is *apparently* inserted into a C—H bond located in an ortho position (reaction 67). The required ortho orientation was recognized as early as 1904 when Sachs and Hilpert<sup>74</sup> proposed that ‘all aromatics which have a

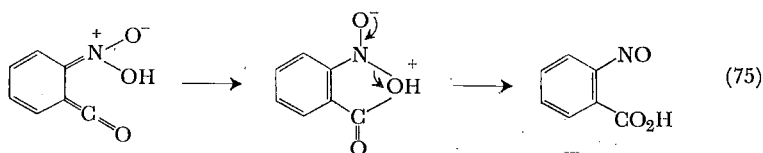
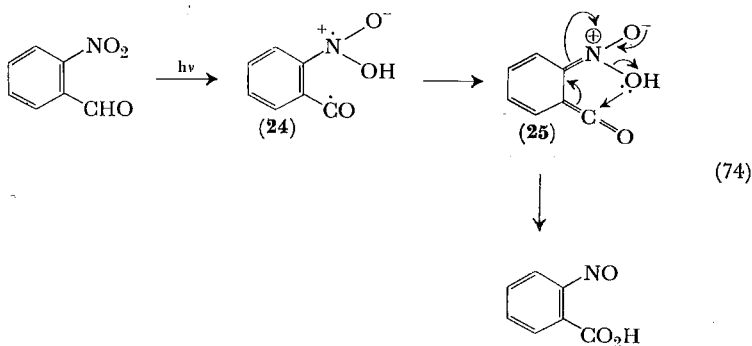


hydrogen ortho to a nitro group will be light sensitive’. Representative examples of this intramolecular oxidation-reduction process are shown in reactions 68–74.

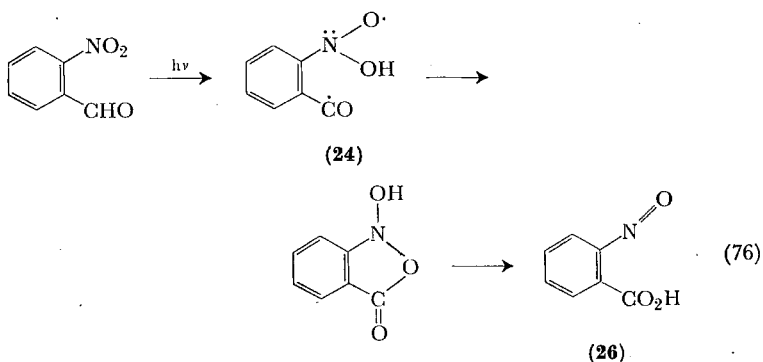


There are several mechanisms which one can write to account for these products. Nitrogen-oxygen bond cleavage and subsequent oxygen atom insertion into the C—H bond has been suggested<sup>38</sup> (cf. section III.D). The best alternative, preliminary transfer of a hydrogen atom to the nitro group, appears to have first been suggested by Tanasescu<sup>59</sup> and more recently by Berson and Brown<sup>60</sup>. The concept was expanded by de Mayo and Reid<sup>80</sup> who utilized initial hydrogen abstraction as a means of rationalizing several photolytic rearrangements of aryl nitro compounds; an example of

their mechanism is shown for the *o*-nitrobenzaldehyde reaction (reaction 74). The final step in reaction 74 is made clearer when represented in a step-wise fashion (reaction 75).

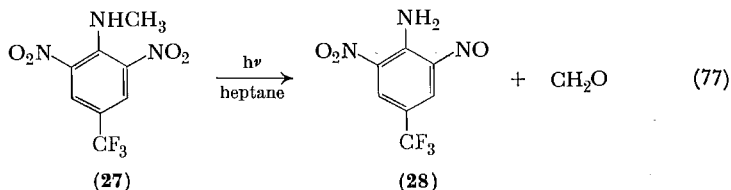


The same reaction may be written in a slightly different fashion (reaction 76) in order to emphasize its possible analogy to a mechanism (reactions 63–66) previously suggested for *intermolecular* oxidation-reduction.

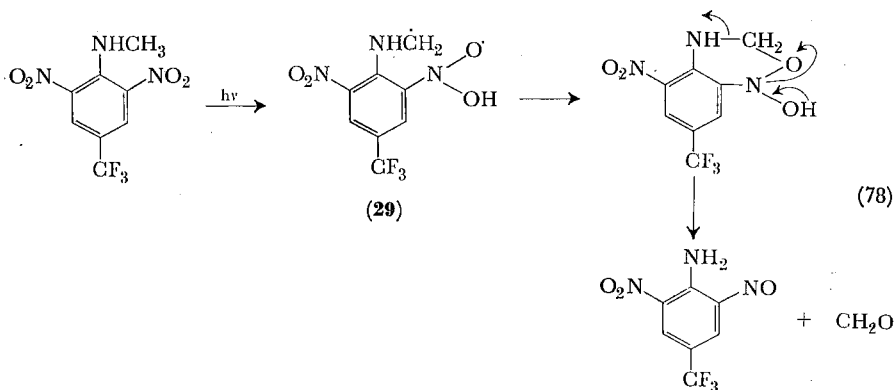


When the odd electrons in **24** are paired, one might consider **24** to be just another representation of the ketene **25**. However, the approach taken in reaction 76 does suggest that a ketene should not be required for this type of reaction, a supposition borne out by the

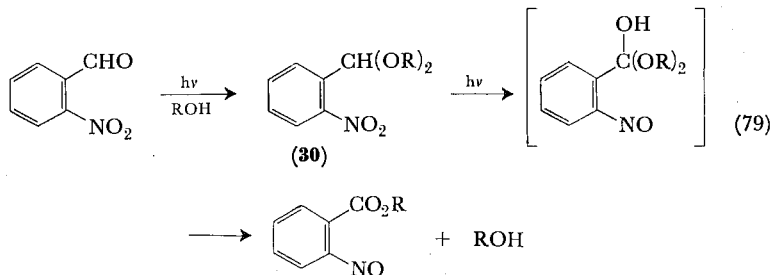
recent observation<sup>81</sup> of reaction 77. (One has to note that collapse of **25** to the acid **26** must be much more rapid than attack by solvent, because photolysis in *i*-propyl alcohol leads to acid and not ester (see discussion below).) A ketene intermediate is plainly



impossible for reaction 77, but coupling of the diradical **29** readily rationalizes these results (reaction 78).

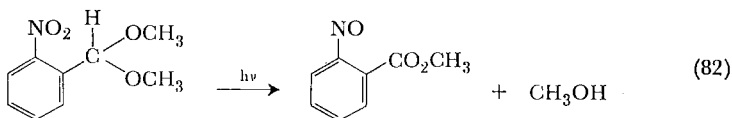
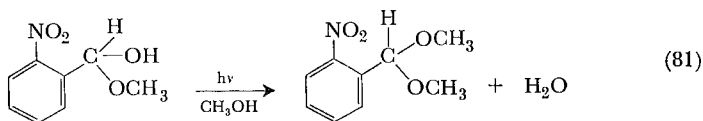
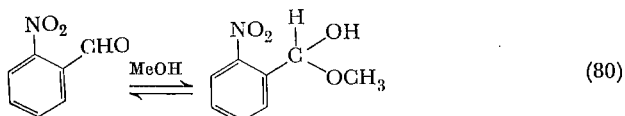


A piece of data which at one time gave credence to ketene formation was the observation that the ester of *o*-nitrosobenzoic acid is formed when the aldehyde is irradiated in alcoholic solution. However, the evidence now available is no longer compatible with the supposition of a ketene precursor of the ester. In 1910, Bamberger and Elger<sup>79</sup> proposed the sequence shown in reaction 79 to explain



ester formation. They were able to show that *ortho* and *para* nitrobenzaldehydes, when dissolved in alcohol, could be converted by light to their acetals under conditions where dark reactions were negligible. Furthermore, the *ortho* acetal **30** (but not the *para* isomer) could be shown to rearrange to the ester (reaction 73) upon irradiation. *Of great interest was the observation that *i*-propyl alcohol as solvent gave mainly acid as product with little ester; it was therefore suggested that two different reaction pathways were operative for the *o*-nitrobenzaldehyde rearrangement, one leading to acid and one leading to ester.*

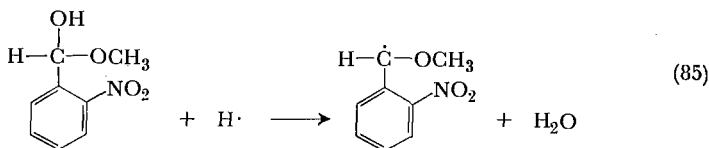
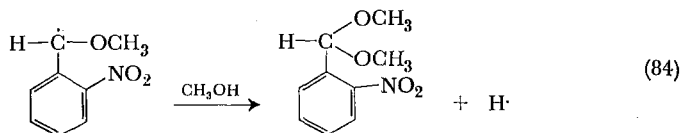
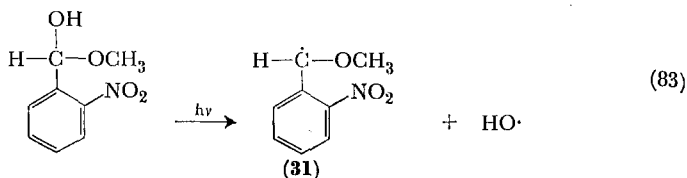
Support for this proposal has recently come forth in the work of Mauser and Heitzer<sup>82</sup> who have observed that both cyclohexane and freshly prepared *i*-propyl alcohol solutions of *o*-nitrobenzaldehyde show a band in the ultraviolet at 3000 Å which is absent in methanol or long-standing (few weeks) *i*-propyl alcohol solutions. They suggest that hemiacetal formation is a rapid dark reaction in methanol and that it is the hemiacetal which is photolytically converted to acetal and then to nitroso ester (reactions 80–83). Since hemiacetal formation is slow in *i*-propyl alcohol, only the acid is formed.



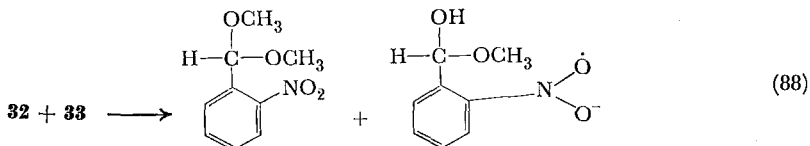
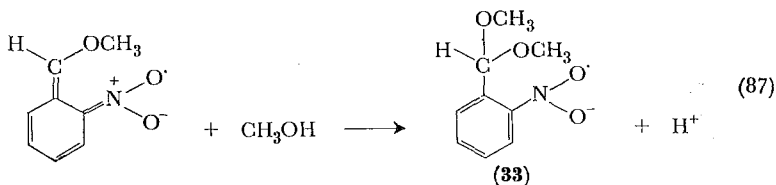
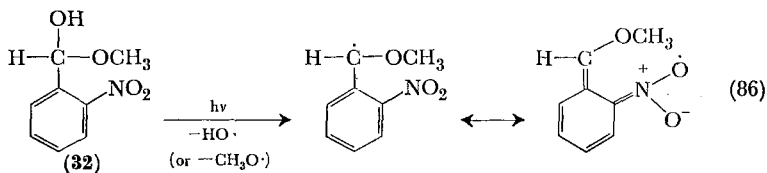
The rearrangement of the acetal to nitroso ester is straightforward and may be readily rationalized along the lines already discussed. However, the photolytic formation of acetal (reaction 81) requires a somewhat different explanation. It is claimed<sup>82</sup> that the rate of this reaction is about thirty times greater than the rate at which *o*-nitrobenzaldehyde forms *o*-nitrosobenzoic acid in cyclohexane. Since the latter reaction has been shown<sup>76</sup> to have a quantum yield of 0.5, a radical chain process is implicated. Furthermore, the authors detect an esr signal when the aldehyde is photolyzed in methanol,

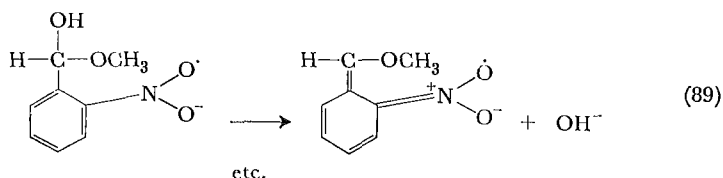


and attributed it to structure **31**. They propose reactions 83–85 to account for these results.

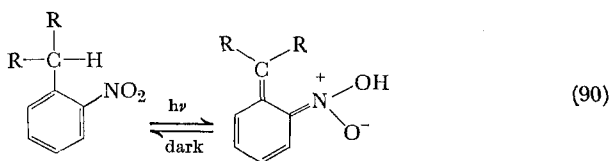


To our knowledge, reaction 84 is without precedent in free radical chemistry and a more attractive alternative can be written (reaction 86–89) which is based upon recent studies<sup>83–85</sup> of nitroaromatic radical anions.



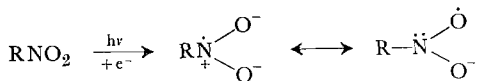


There is a large amount of data now in the literature concerning the photochromism of suitably substituted nitroaromatics; the substrates all have in common a benzylic hydrogen *ortho* to the nitro group and it is well established<sup>86-88</sup> that the colored transients have an *aci*-nitro structure (reaction 90). An interesting exception is the recent report by Bluhm and Weinstein<sup>89</sup> (cf. section III.K).

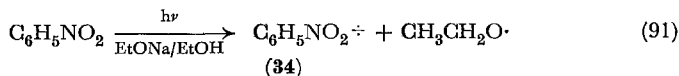


Although aliphatic nitro compounds should, in theory, be equally capable of abstracting hydrogen atoms, the only relevant experiments are those referred to in section III.E.

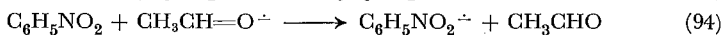
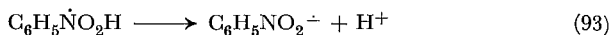
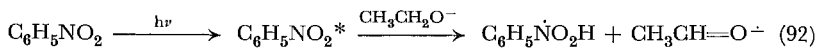
### J. Radical Anion Formation



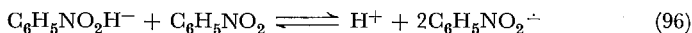
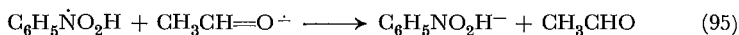
In 1963, Ayscough and Sargent<sup>90</sup> noted that upon irradiation of nitrobenzene in basic alcoholic solutions, an esr signal developed which was characteristic of the radical anion of nitrobenzene, (34) (reaction 91).



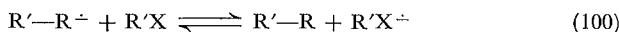
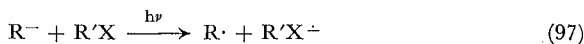
Although this appeared to be an example of what one might term 'electron abstraction' by the photoexcited nitro group, Russell and Geels<sup>91</sup> suggested that the radical anion actually came about *via* initial hydrogen abstraction (reactions 92, 93, 94 or 95, 96).



or



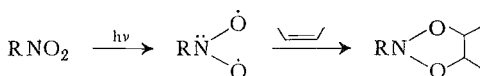
More recently, Russell and Danen<sup>85</sup> have observed that photolysis of *m*-nitrobenzyl chloride in the presence of the 2-nitro-2-propyl anion produces the radical anion of *m*-nitrobenzyl chloride; with *p*-nitrobenzyl chloride, a chain reaction follows the electron transfer and results in alkylation. Similar observations were made with 2-nitro-2-propyl halides (reactions 97–100).



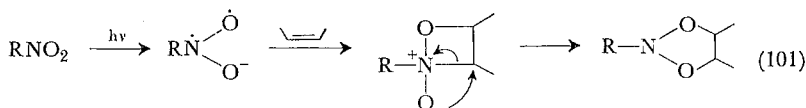
etc.

(R'X = nitrobenzyl chloride)

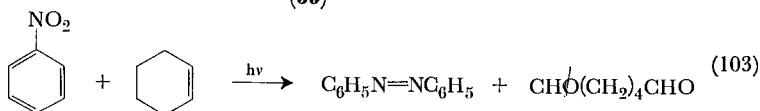
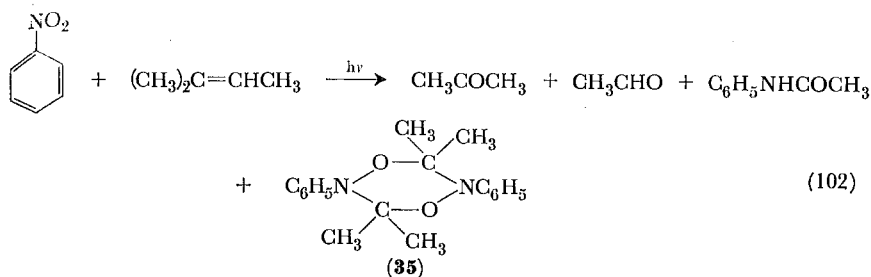
### K. Nitro Photocycloaddition



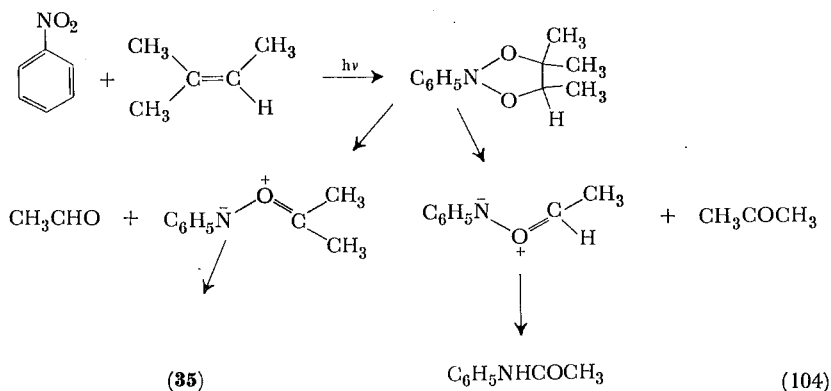
Before listing the reactions which appear to proceed *via* this primary act, it is worth noting that a photochemical process which would be more analogous to oxetane formation in the carbonyl series, would be N—O photocycloaddition<sup>\*</sup>; since the initial product of such a reaction could easily rearrange to the product of O—O photocycloaddition, a distinction between these cannot be made at this time (reaction 101),



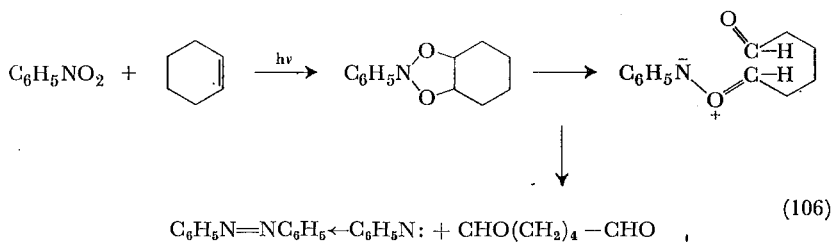
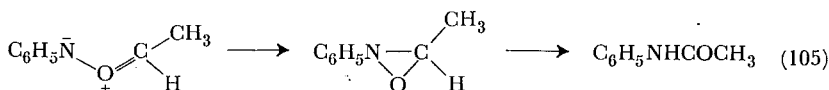
This primary act was first suggested by Buchi and Ayer<sup>92</sup> as a means of explaining the reaction of nitrobenzene with 2-methyl-2-butene (reaction 102) and cyclohexene (reaction 103). The authors



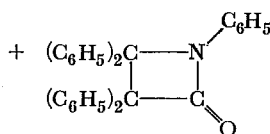
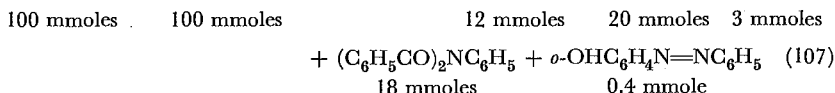
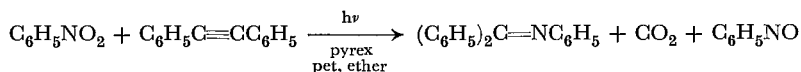
noted the similarity of these reactions to ozonolysis and suggested an initial adduct analogous to an ozonide. The suggested mechanism is shown in reaction 104. The formation of acetanilide could proceed



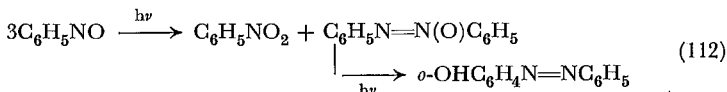
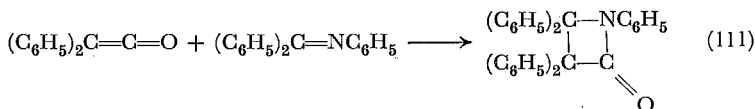
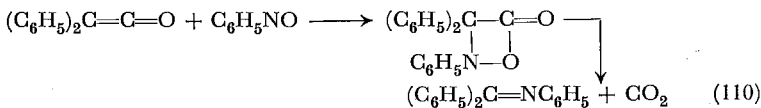
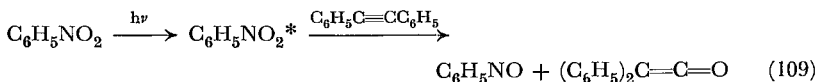
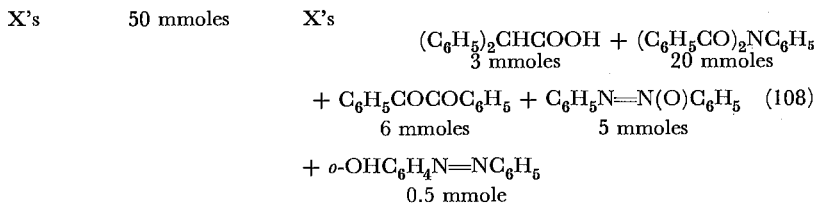
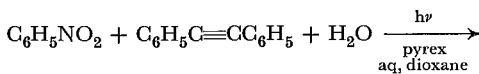
through formation of the oxazirane (reaction 105) and azobenzene was suggested to have been generated from phenyl nitrene (reaction 106).

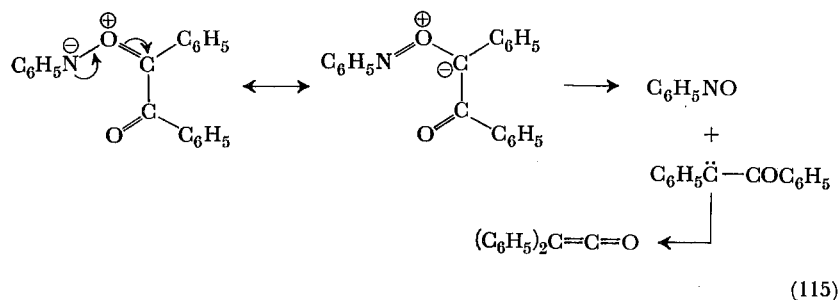
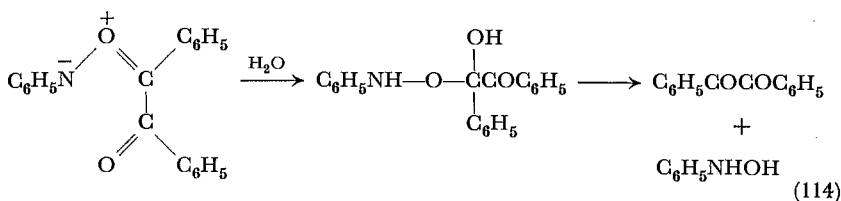
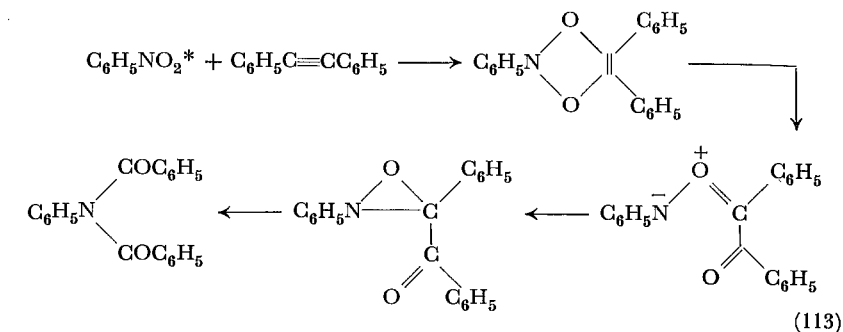


Photolysis of nitrobenzene in the presence of diphenylacetylene has been found<sup>93</sup> to give an even more complex mixture of products (reactions 107 and 108), Scheinbaum suggests the mechanism depicted in reactions 109–114. No suggestion was made as to how



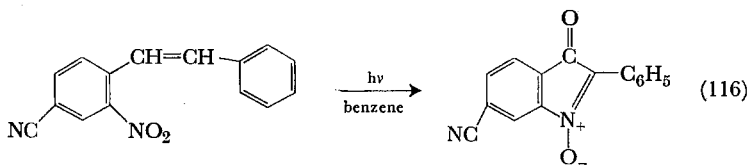
0.9 mmole

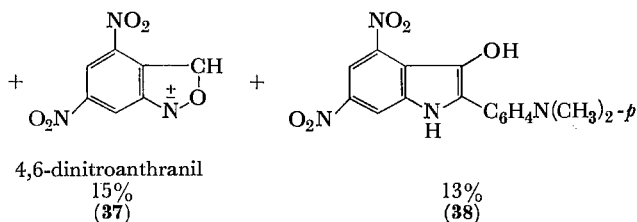
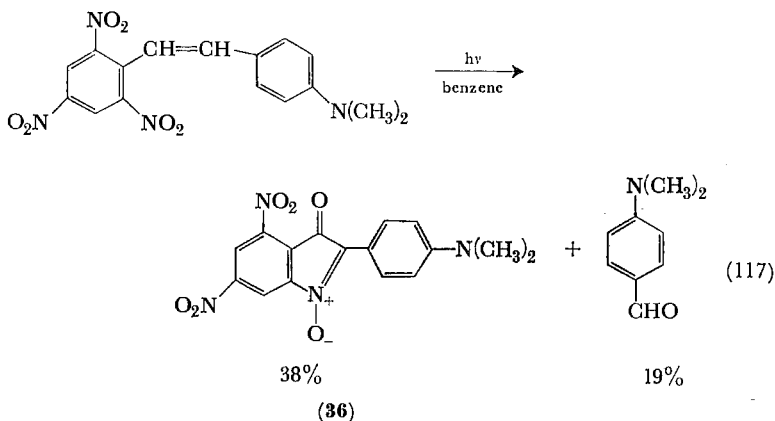




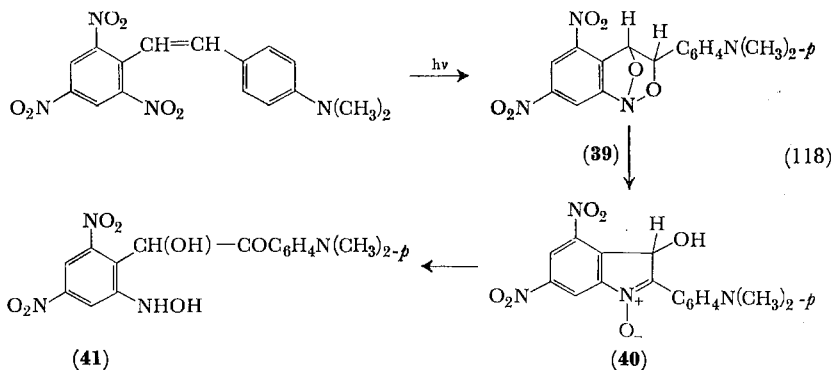
nitrosobenzene and diphenylketene might have been formed (cf. reaction 109); reaction 115, a modification of reaction 113, is one conceivable possibility. Thus initial photocycloaddition (reactions 113 and 115) accounts well for the products.

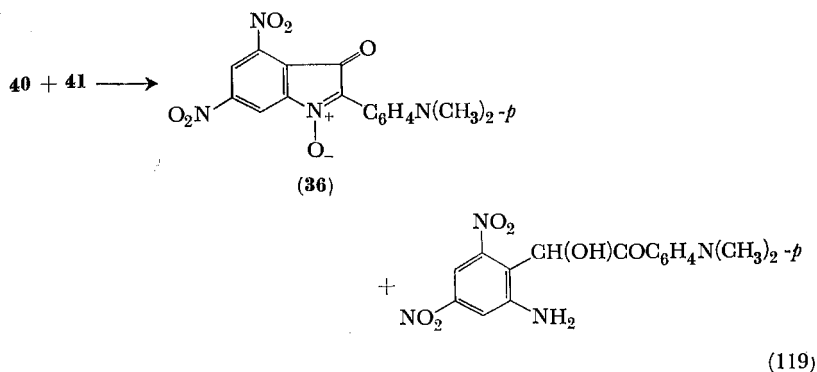
Intramolecular cycloaddition has been proposed by Splitter and Calvin to rationalize the photolytic rearrangement of *o*-nitrostilbenes to 2-phenylisatogens<sup>94-96</sup> (reactions 116 and 117). Using ultraviolet



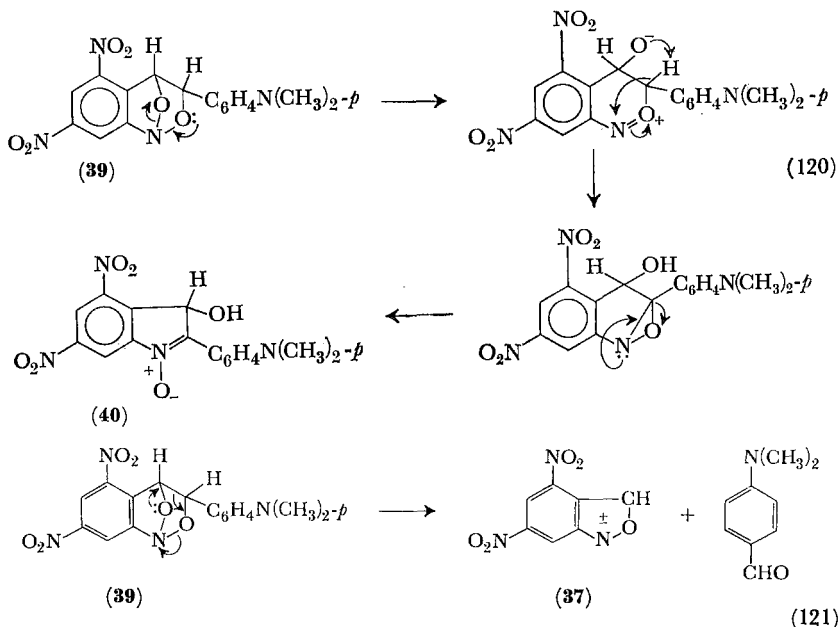


spectroscopy, these workers were able to detect an intermediate which went on to form the isatogen **36** in a dark reaction; they suggest that this intermediate is **40**, and that it is oxidized to the isatogen by an intramolecular oxidation-reduction reaction involving its hydrolysis product, **41**. The adduct **39** is suggested as the precursor of **40** (reactions 118 and 119). The indoxyl **38** is rationalized as being formed by reduction of the isatogen.



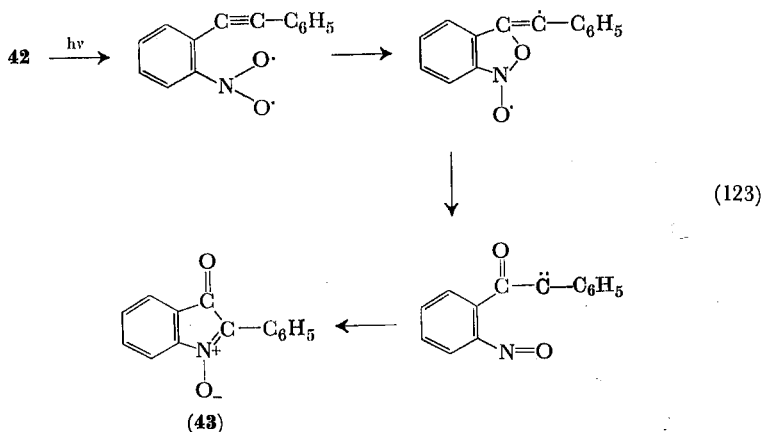
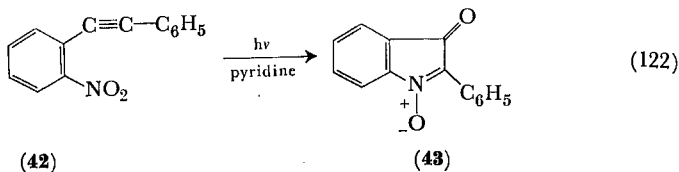


Actually, the formation of **37**, *p*-dimethylaminobenzaldehyde, and the proposed intermediate **40**, are all very nicely accounted for by the adduct **39**; formation of the intermediate is detailed in reaction 120 and the other products in reaction 121.

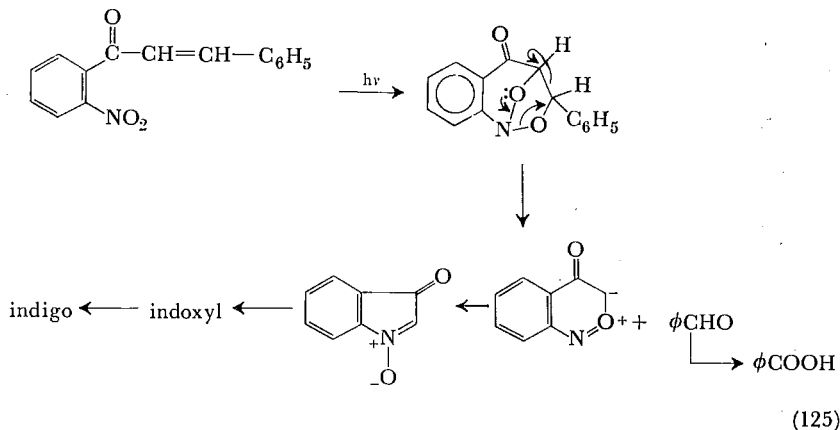
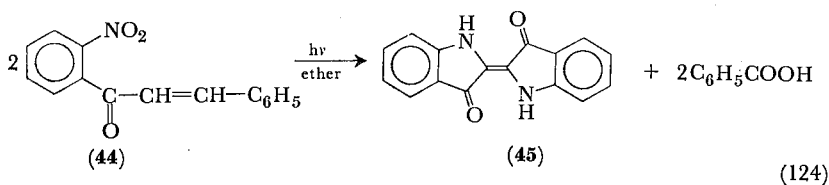


Several other types of substrates have been found to yield isotogens upon irradiation<sup>97-99</sup>. One of the more fascinating rearrangements is that of *o*-nitrotolan (42) to 2-phenylisatogen (43)<sup>98</sup> (reaction 122). One possible mechanism is presented in reaction 123.

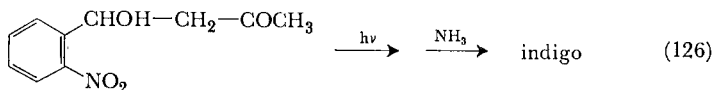




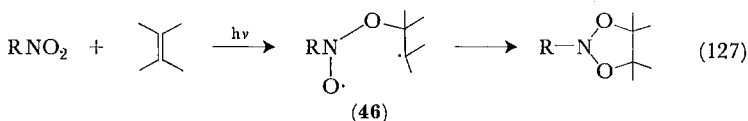
The isolation of the indoxyl, **38**, by Splitter and Calvin could be the key to an explanation for the formation<sup>100</sup> of indigo (**45**) from



**44** (reaction 124). Indoxyl is known to air oxidize to indigo and could be formed as in reaction 125. An alternate photochemical route to indigo has been reported<sup>101</sup> (reaction 126).

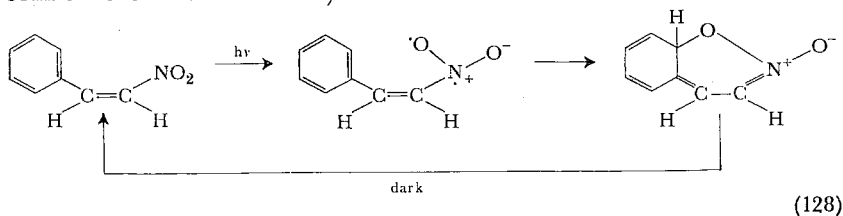


When viewed in detail, the formation of the cycloadducts in a *completely* concerted fashion seems improbable since the diradical excited state precursor has its two unpaired electrons in orthogonal orbitals. This would suggest that a more fundamental approach to the primary act would be a hypothetical addition of the diradical to a  $\pi$  system to produce a second transient diradical **46** (reaction 127). It has already been suggested (reaction 15, section III.D) that



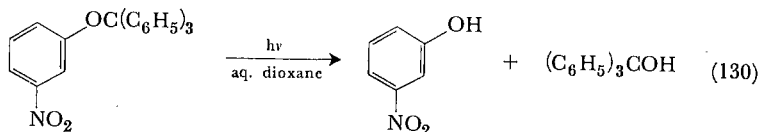
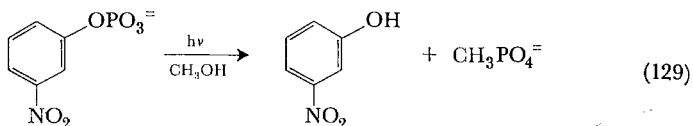
an adduct similar to **46** may be responsible for the formation of nitrosobenzene from nitrobenzene. Another intermolecular example was the postulated addition to the acetylene linkage (reaction 123). Chapman has proposed an intramolecular analog (reaction 40, section III.H).

With this in mind, the recent report of Bluhm and Weinstein is of great interest<sup>89</sup>. They find that  $\beta$ -nitrostyrene derivatives are photochromic as long as the aryl and nitro groups are *cis* to each other. [Whatever is causing these compounds to be photochromic could also be the reaction responsible for the fact that *cis*- $\beta$ -nitrostyrene has never been photodimerized nor added successfully to olefins (section III.G).] Though there is as yet no evidence published which would support this postulate, it may well be addition of the nitro group to the aromatic ring which is resulting in a colored product (reaction 128). If true, this reaction would constitute further evidence for a fundamental primary act in which the excited nitro group adds stepwise to unsaturated systems (in this case, resulting in concomitant C=N formation).



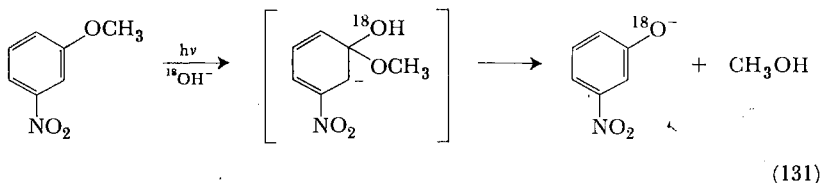
#### IV. PHOTOINDUCED NUCLEOPHILIC SUBSTITUTION OF NITROAROMATICS

It is not yet clear how essential the nitro group is to the reactions described below. In the case of photochemical solvolyses<sup>102</sup> (reactions 129 and 130), there is evidence that the presence of other electron withdrawing substituents on the aromatic ring will also bring about the phenomena observed<sup>103</sup>. However, it may well be more than



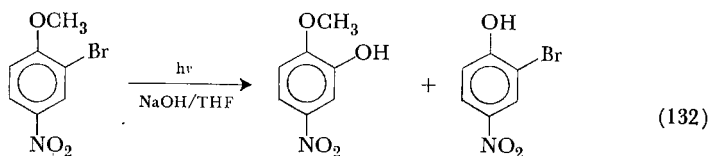
coincidence that all of the photochemical nucleophilic aromatic substitutions so far reported, take place with nitroaromatics; for this reason, I have included representative examples and references in this review.

The first observation of unusual reactivity in a nitroaromatic, directly attributable to photoinduced nucleophilic attack on the benzene ring, involved *m*-nitroanisole<sup>104</sup>. Recent experiments<sup>105</sup> with oxygen-18 labeled base indicate that the initial attack is on the ring carbon and not on the carbon of the methoxy group (reaction 131). Further support for this mechanism comes from the flash



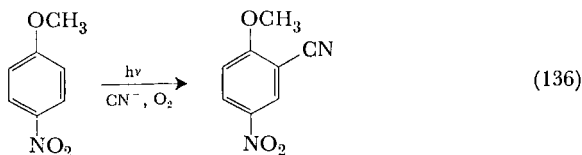
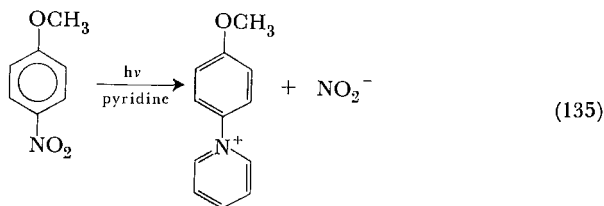
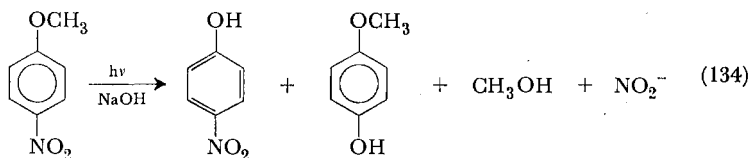
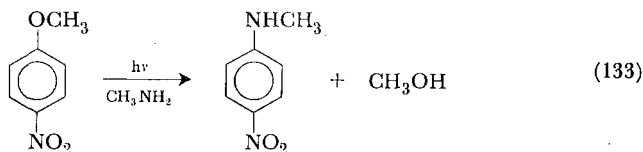
photolysis of basic solutions of 3,5-dinitroanisole<sup>106</sup>, whereby an ultraviolet absorption spectrum attributable to the sigma complex is observed. Interestingly, 2-bromo-4-nitroanisole reacts in a similar fashion but 3-nitrobromobenzene is reported to be unreactive<sup>107</sup> (reaction 32).

The nature of the nucleophile plays a large role in determining the site of attack on the ring. Methylamine<sup>108</sup>, hydroxide ion<sup>108,109</sup> and

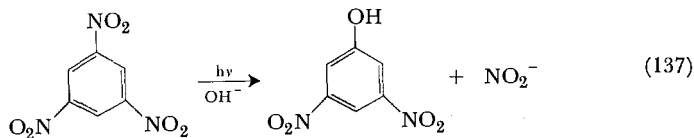


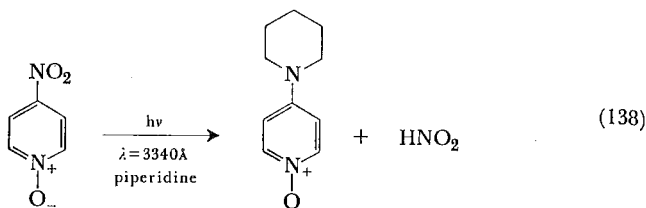
major product

pyridine<sup>109</sup> give a variety of products with *p*-nitroanisole (reactions 133–135). Still a third type of reaction occurs when cyanide ion is the nucleophile<sup>110</sup> (reaction 136).

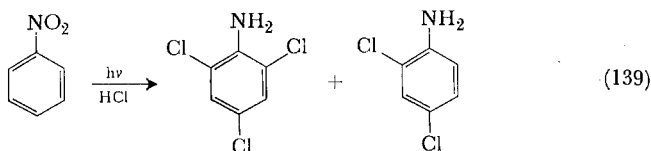


Other examples<sup>111,112</sup> of nucleophilic attack on the carbon bearing nitro groups are shown in reactions 137 and 138.





Letsinger and Wubbels recently published<sup>113</sup> on the reaction of nitrobenzene with conc. hydrochloric acid (reaction 139). Nitration



of nitrobenzene with nitric acid during irradiation with ultraviolet light has been shown to give a mixture of meta and para dinitrobenzene<sup>114</sup>.

## V. ULTRAVIOLET SPECTROSCOPY OF NITROSO COMPOUNDS

Since this subject is extensively reviewed in Chapter 3 of this volume, only the salient features of the ultraviolet absorption spectra of nitroso compounds will be treated here.

Nitroso aliphatics show characteristic absorption in three regions: *ca.* 6900, 2700 and 2200 Å. Both of the long-wavelength bands have been assigned to the promotion of a non-bonding (*n*) electron to an anti-bonding ( $\pi^*$ ) orbital. The red band (6900 Å) is due to an  $n_N \rightarrow \pi^*$  transition<sup>115, 116</sup> whereas the 2700 Å band has been assigned to an  $n_O \rightarrow \pi^*$  transition<sup>116</sup>. Aromatic nitroso compounds also show a band in the visible region (*ca.* 7000 Å) which is likewise assigned to an  $n_N \rightarrow \pi^*$  transition<sup>117, 118</sup>; for this class of compounds, the  $n_O \rightarrow \pi^*$  band appears to be buried under bands attributed to the aromatic ring.

From these data, one can say that the lowest lying singlet and triplet states of nitroso compounds are  $n$ ,  $\pi^*$  with most of the photochemistry discussed in section V resulting from an initial  $n_N \rightarrow \pi^*$  transition. The obvious exception is the resistance of aryl nitroso compounds to photolysis by red light (*cf.* section V.B). Nothing is yet known of the possible involvement of triplet states in nitroso photochemistry.

## VI. PRIMARY PHOTOCHEMICAL PROCESSES OF THE NITROSO GROUP

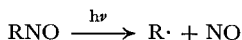
### A. Compilation of Primary Photochemical Acts

Listed in Table 2 are the primary processes which have been suggested to explain the photochemistry of nitroso compounds. Relatively little work has been done in this area by comparison with the nitro group.

TABLE 2. Primary photochemical processes of nitroso compounds.

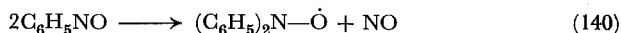
Reaction	Classification
1. $\text{RNO} \xrightarrow{h\nu} \text{R}\cdot + \text{NO}$	Photodissociation
2. $\text{RNO} + \text{R}'\text{H} \xrightarrow{h\nu} \text{RNOH} + \text{R}'\cdot$	Hydrogen abstraction
3. $\text{R}_2\underset{\text{NO}}{\underset{ }{\text{C}}}-\text{CHR}_2 \xrightarrow{h\nu} \text{R}_2\text{C}=\text{CR}_2 + \text{HNO}$	Photocycloelimination
4. $\text{R}-\underset{\text{NO}}{\underset{ }{\overset{\text{Cl}}{\text{C}}}}-\text{CR}_3 \xrightarrow{h\nu} \text{R}-\underset{\text{NO}}{\underset{ }{\dot{\text{C}}}}-\text{CR}_3 + \text{Cl}\cdot$	Halogen atom expulsion

### B. Photodissociation



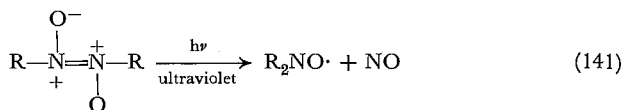
### I. Nitroxide formation

The formation of nitroxides by the irradiation of aromatic and aliphatic nitroso compounds is now well established. The reaction was first observed with nitrosobenzene using esr to detect the product<sup>120</sup> (reaction 140).

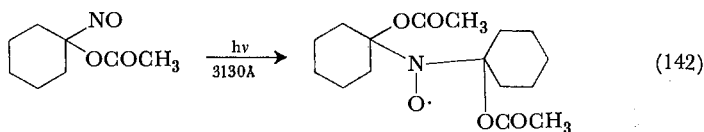


Mackor, Wajer, de Boer and van Voorst<sup>121</sup> have since found that this reaction is general for aliphatic and aromatic nitroso compounds; the wavelength of light required to bring about formation of the nitroxide is dependent, however, on the nitroso compound. Thus primary, secondary and tertiary nitrosoalkanes can be converted to nitroxides by red light ( $\lambda > 6600 \text{ \AA}$ ) whereas nitrosobenzene requires irradiation with ultraviolet light. Since many nitroso compounds exist at room temperature in equilibrium with their azodioxy<sup>122</sup>

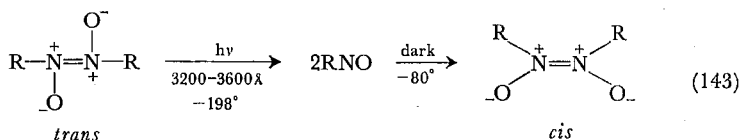
dimers, there has been some suggestion<sup>123,124</sup> that these dimers are responsible for nitroxide formation (reaction 141). Because the



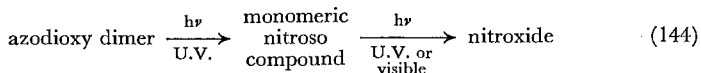
dimers do not absorb visible light, this reaction would, at best, explain only the formation of nitroxide due to ultraviolet light. Recent data<sup>125</sup> now indicate that *exclusively monomeric* nitroso substrates give rise to nitroxides when irradiated in the u.v. (reaction 142) and that the dimers are cleaved to monomers upon photolysis (reaction 143). (Reaction 143 has been used to make exclusively



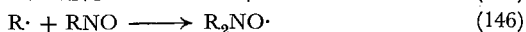
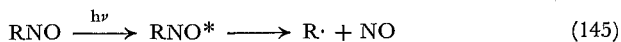
(monomeric)



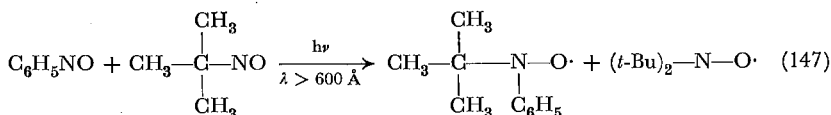
*cis*-azodioxy dimers.) These data have been interpreted<sup>125</sup> as indicating that nitroxide formation occurs exclusively from monomeric nitroso compounds (reaction 144).



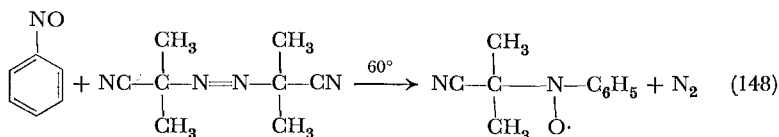
The simplest explanation for nitroxide formation from nitroso compounds is the sequence of reactions shown in reactions 145 and 146. Strong support for this view comes from the report<sup>121</sup> that



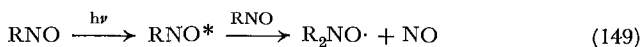
mixed aryl aliphatic nitroxides can be made using red light (i.e. light which does not decompose nitrosobenzene) (reaction 147).



Nitroso compounds have been shown<sup>121,126</sup> to add alkyl radicals in this fashion (reaction 148).

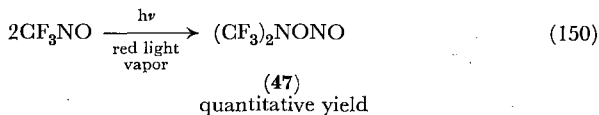


The possibility of collision between a long-lived excited state of the nitroso compound and a second molecule with the concomitant formation of nitroxide has been proposed and it is felt that this mechanism still warrants consideration<sup>121</sup> (reaction 149).

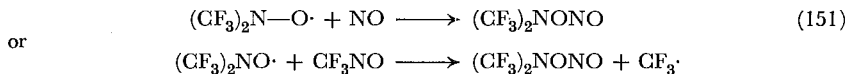
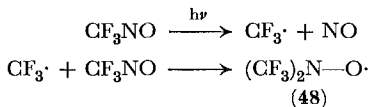


## 2. N-Nitritoamine formation

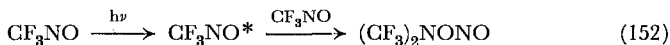
When perfluoronitrosomethane is irradiated with red light, compound **47** is the principle product observed<sup>127,128</sup> (reaction 150).



The mechanism which has been put forth to explain this reaction involves photodissociation as the primary act (reaction 151)<sup>127</sup>.



However, a primary act (reaction 152) reminiscent of that suggested to explain nitroxide formation (e.g. reaction 149) has also been proposed<sup>128</sup>.



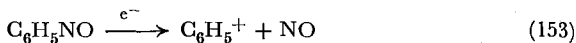
The fact that bis(trifluoromethyl)nitroxide (**48**) has not been detected in this reaction and the absence of  $\text{CF}_3\text{NF}_2$  when perfluoronitrosomethane is irradiated in the presence of  $\text{N}_2\text{F}_4$  has been taken as evidence against an initial photodissociation<sup>129</sup>. On the other hand, **48** has recently been isolated and does indeed react with



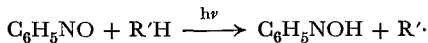
nitric oxide to give the nitrite **47**<sup>130</sup>. Haszeldine has recently<sup>131</sup> reaffirmed his belief in the photodissociation mechanism, at least as regards ultraviolet induced reactions.

### 3. Mass spectral data

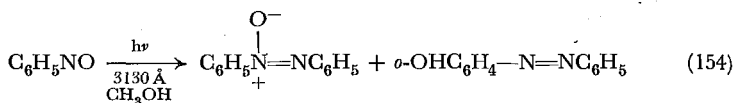
The base peak in the mass spectrum of nitrosobenzene appears at 77 m/e, corresponding to the loss of NO from the parent ion (reaction 153)<sup>132</sup>. Experience with a number of systems suggests that facile cleavage of this sort in the mass spectrum *usually* is mirrored in the photochemistry of the molecule.



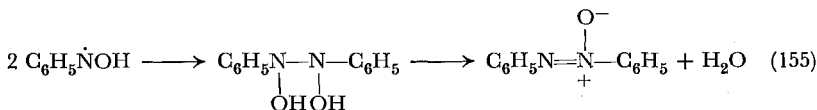
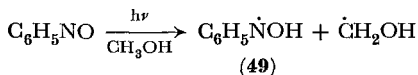
### C. Hydrogen Abstraction



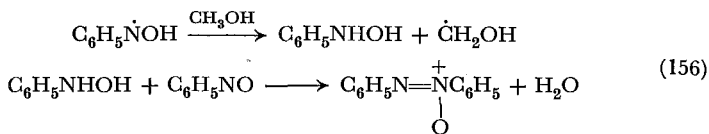
Nitrosobenzene, upon irradiation with ultraviolet light, has been shown to form azoxybenzene and 2-hydroxyazobenzene as the major products (reaction 154).



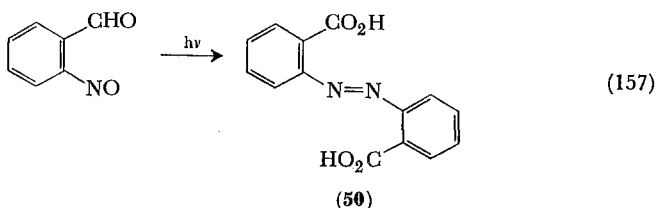
When the reaction is followed by ultraviolet absorption spectroscopy, isobestic points are observed which have been attributed<sup>133</sup> to a radical intermediate **49** which dimerizes and upon subsequent dehydration leads to azoxybenzene (reaction 155).



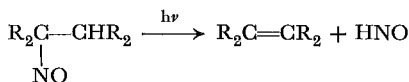
An alternative to the proposed dimerization of **49** would be a second hydrogen abstraction to give phenylhydroxylamine, a compound known<sup>134</sup> to react rapidly with nitrosobenzene to produce azoxybenzene (reaction 156).



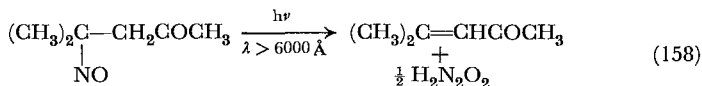
When nitrosobenzene is dissolved in 95% ethanol and irradiated in the presence of oxygen for several days, a wide variety of products are observed<sup>135</sup> which are quite different from the anaerobic reduction described above. A reaction which possibly fits into the general category under discussion is shown in reaction 157; structure **50** is formed in addition to much tar<sup>136</sup>.



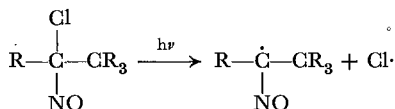
#### D. Photocycloelimination



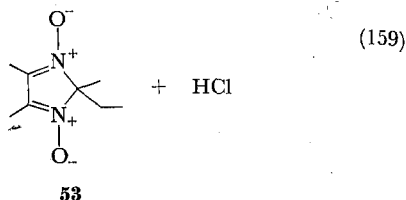
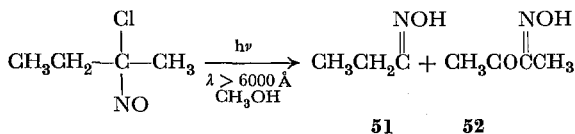
This process was suggested as a means of accounting for the photodecomposition of nitrosoisopropylacetone to mesityl oxide (reaction 158); the quantum yield for disappearance of the nitroso compound is unity<sup>137</sup>.



#### E. Halogen Atom Expulsion

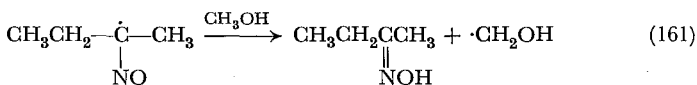
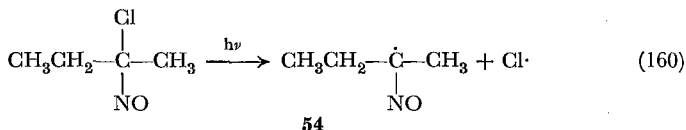


In 1938, Mitchell and Cameron reported on the photolysis of 2-chloro-2-nitrosobutane; the major products were HCl, **51**, **52**, and **53** (reaction 159)<sup>138</sup>. The dinitrone **53** has been shown<sup>139</sup> to



form in a secondary dark reaction between **51** and **52**. Several other chloronitroso compounds have been shown to give oximes upon irradiation<sup>140</sup>.

Although the loss of HCl was originally suggested as the primary act for these reactions,<sup>138</sup> initial expulsion of a halogen atom seems more likely<sup>141</sup>. Hydrogen abstraction by the resulting radical **54** would then lead directly to the oxime (reactions 160, 161). The formation of **52** remains anomalous and may conceivably be related to observations made by Chapman in the nitro series (cf. section III.H).



## VII. ACKNOWLEDGMENTS

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## IX. ADDENDA

The following articles appeared after completion of this chapter. Of particular note is the paper by Charton and de Mayo<sup>161</sup> in which is reported the isolation of a cycloadduct corresponding to that discussed in section III.K.

142. "Photoreactions of Aromatic Molecules", E. Havinga, R. O. De Jongh, and M. E. Kronenberg, *Helv. Chim. Acta*, **50**, 2551 (1967).
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145. "Photodissociation of Nitroso Dimers", A. L. Bluhm and J. Weinstein, *Nature*, **215**, 1478 (1967).
146. "Preparation of  $\alpha$ -Naphthylamine by the Photochemical Reduction of  $\alpha$ -Nitronaphthalene", S. Hashimoto, H. Fujii, and J. Sunamoto, *Kogyo Kagaku Zasshi*, **70**, 316 (1967).
147. "c-Nitroso Compounds. II. On the Photochemical and Thermal Formation of Nitroxides from Nitroso Compounds as studied by ESR", Th. A. J. Wajer, A. Mackor, Th. J. deBoer, and J. D. W. van Voorst, *Tetrahedron*, **23**, 4021 (1967).
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152. "Photochemical Transformations II. Photochemistry of 6-Nitrocholesteryl Acetate and Related Compounds", G. E. A. Coombes, J. M. Grady, and S. T. Reid, *Tetrahedron*, **23**, 1341 (1967).

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156. "Nitroxide Radicals Formed in the Liquid Phase by Photolysis of Nitro Compounds. Nitroalkanes in Polar Solvents", C. Chachaty and A. Forchioni, *Tetrahedron Lett.*, **1968**, 1079.
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## CHAPTER 5

# Methods of formation of the nitroso group and its reactions\*

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I. INTRODUCTION . . . . .	216
II. PREPARATIVE METHODS . . . . .	217
A. Nitric Oxide and Radicals . . . . .	217
B. Irradiation of Nitrosyl Halide and Alkanes . . . . .	219
C. Pyrolysis and Photolysis of Nitrite Esters . . . . .	220
D. Oxidative Nitrosation (Baudisch Reaction) . . . . .	222
E. Nitrosation of Tertiary Aromatic Amines . . . . .	223
F. Nitrosation of Secondary Aromatic Amines . . . . .	223
1. Fischer-Hepp reaction . . . . .	223
2. Based catalysed migration of the nitroso group from nitrogen to carbon . . . . .	225
G. Nitrosation of Primary Aromatic Amines . . . . .	225
H. Nitrosation of Phenols . . . . .	226
I. Nitrosation of Aromatic Ethers . . . . .	226
J. Nitrosative Decarboxylation . . . . .	227
K. Nitrosation of Olefins . . . . .	229
1. Nitrous acid, nitrites, nitrogen oxides and nitrosamines . . . . .	229
2. Nitrosyl halides and nitrosyl sulfuric acid . . . . .	230
3. Dehydrohalogenation of olefin nitrosohalides . . . . .	232
L. Nitrosation of Phenols and Heterocycles with Nitrite Esters and Alkoxides . . . . .	233
M. Organometallic Compounds and Nitrosyl Chloride . . . . .	234
N. Geminal Nitrosohalides from Oximes . . . . .	235
O. Esters of Geminal Nitrosoalcohols from Oximes . . . . .	238
P. Oxidation of Dioximes . . . . .	238
Q. Oxidation of Hydroxylamines . . . . .	240
R. Oxidation of Primary Amines . . . . .	241

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S. Oxidation of Secondary Amines . . . . .	242
T. Oxidation of Tertiary Amines . . . . .	243
U. Oxidation of Nitrones and Schiff Bases . . . . .	243
V. Reduction and Deoxygenation of Nitro Compounds . . . . .	244
W. Nef Reaction . . . . .	248
X. Pyrolysis of Heterocycles . . . . .	249
Y. Electrolysis of Oxime Salts . . . . .	250
Z. Condensation Reactions . . . . .	250
Z <sub>1</sub> . Nitroso Compounds from Diazo and Diazonium Compounds . . . . .	251
Z <sub>2</sub> . Natural Occurrence . . . . .	251
III. STRUCTURE AND REACTIONS . . . . .	252
A. Dimerization . . . . .	252
B. Isomerization to Oximes . . . . .	255
C. Nitrosoaromatic Amine Zwitterions . . . . .	258
D. Activation of Other Substituents . . . . .	259
E. Reduction . . . . .	260
F. Deoxygenation . . . . .	263
G. Oxidation . . . . .	264
H. Free Radicals . . . . .	265
I. Monoolefins . . . . .	266
J. Acetylenes and Arynes . . . . .	268
K. Thioketones, Phosphorous Ylids, Azomethine Derivatives . . . . .	268
L. Diazoalkanes . . . . .	269
M. Conjugated Dienes . . . . .	270
N. Compounds with Active Hydrogen . . . . .	271
O. Complexes with Metal Salts and Lewis Acids and Metal Chelates . . . . .	273
P. Methylene and Methynyl Groups in Olefins, Schiff Bases, Carbonyl Compounds . . . . .	275
Q. Grignard Reagents . . . . .	276
R. Ehrlich-Sachs Reaction . . . . .	277
S. Amines, Hydroxylamines, Hydrazines . . . . .	278
T. Substitution Reactions in Aromatic Nitroso Compounds . . . . .	283
U. Cleavage of C-nitroso Bond . . . . .	284
V. Pyrolytic and Photolytic Disproportionation . . . . .	285
W. Miscellaneous Reactions of Nitroso Compounds . . . . .	286
1. Conjugate addition . . . . .	286
2. Fragmentation . . . . .	286
3. Reactions promoted by the presence of nitrosobenzene . . . . .	287
IV. REFERENCES . . . . .	287

## I. INTRODUCTION

Appreciation of the chemistry of the C-nitroso group has developed slowly notwithstanding its extensive literature. Undoubtedly a contributing factor has been its absence, except for a few examples, in naturally occurring materials.

In the past decade there have been several important developments including the nmr analysis of the structural relationship between benzfuroxan and *o*-dinitrosobenzene, the esr determination of nitroso radical-anions, photochemical nitrosations, deoxygenation to a nitrene and addition to dienes which have brought nitroso chemistry to the forefront.

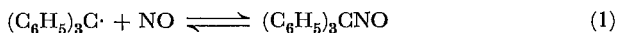
Organic synthesis has been substantially helped by the chemistry of the C-nitroso function but it would appear that it will be even more richly rewarded in the future. Two examples may serve to illustrate. In the first, addition of the nitroso group to a C—H bond adjacent to an olefinic, azomethine or other unsaturated linkage offers a promising method to be developed for introducing a functional group at an  $sp^2$  carbon atom. The second example consists in the emerging chemistry of the nitroso group conjugated with one or more unsaturated linkages and is demonstrated in conjugate addition and valence isomerization reactions of nitroso olefins and in the recently discovered ethynyl nitroso compounds.

A comprehensive presentation<sup>1</sup> of the chemistry of the C-nitroso compounds appeared recently. The present work is intended to be complementary and to include new information in the rapidly growing field.

## II. PREPARATIVE METHODS

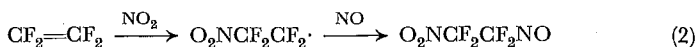
### A. Nitric Oxide and Radicals

In an early recognition of the affinity between nitric oxide and organic radicals, it was assumed that the appearance of a blue color on mixing triphenylmethyl with nitric oxide in ether in the absence of air denoted the presence of triphenylnitrosomethane (equation 1). Reversibility of the reaction was suggested by the disappearance of the blue color and recovery of starting materials on evaporation of the solvent<sup>2</sup>.

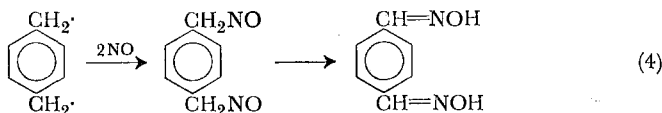
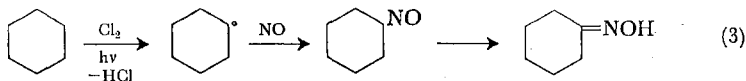


Many reactions which lead to the formation of nitroso compounds are best understood on the basis of a combination of nitric oxide with an appropriate free radical. It is such a combination, for example, which permits nitric oxide to inhibit free radical chain reactions<sup>3</sup>. The formation of the lower molecular-weight nitrosoalkanes has been observed in gas-phase reactions between nitric oxide and the corresponding alkyl group generated *in situ* by the photolysis of an

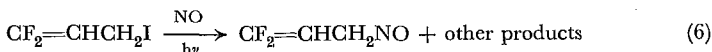
azoalkane<sup>4</sup>, pyrolysis of a dialkyl mercury compound<sup>5</sup>, photolysis of an alkyl halide<sup>6,7</sup>, the addition of a radical such as nitrogen dioxide to an olefin<sup>8</sup> (equation 2), and by other means. It is reported that  $\gamma$ -irradiation of a mixture of carbon tetrachloride and nitric oxide leads to the formation of trichloronitrosomethane<sup>9</sup>.



Nitric oxide readily combines with the cyclohexyl radical which may have been generated by the action of a chlorine atom on cyclohexane<sup>10</sup> (equation 3) and with the reactive diradical form of *p*-xylylene<sup>11</sup> (equation 4).

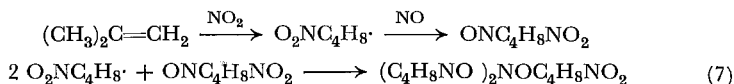


Nitroso olefins in which the substituent is attached to  $sp^2$  carbon are less well-known; nevertheless perfluoronitrosoethylene has been obtained from the reaction between trifluoroiodoethylene and nitric oxide<sup>12</sup> (equation 5). In contrast trifluoronitrosoethylene has not been detected in the reaction mixture obtained from trifluorochloroethylene and nitric oxide<sup>13</sup> and a reaction presumably initiated by nitrogen dioxide gives saturated products instead. Nitroso olefins with the substituent attached to  $sp^3$  carbon have been prepared in a similar way<sup>14</sup> (equation 6) through irradiation of an allylic iodide in the presence of nitric oxide.

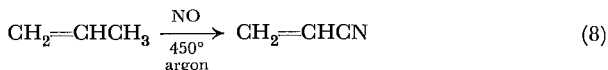


Apparently pure nitric oxide does not react with monoolefins under ordinary conditions<sup>15</sup>; however, a trace of nitrogen dioxide which is usually present will initiate a reaction leading to a mixture of products in which nitro compounds predominate. From isobutylene up to 45% *tris*(nitro-*t*-butyl)hydroxylamine has been

reported<sup>16</sup> (equation 7). The transformation of olefins into nitriles



by nitric oxide at high temperatures is not completely understood<sup>17</sup> (equation 8) and the intermediacy of nitroso derivatives has not been established.



Carbonyl derivatives with the nitroso group attached to the carbonyl carbon are unknown; however,  $\text{CH}_3\text{CONO}$  has been a suggested intermediate in the photochemical oxidation of nitric oxide to nitrogen dioxide in acetone<sup>18</sup>. The formation of nitroso aromatic compounds by the combination of aryl radicals and nitric oxide apparently has not been reported.

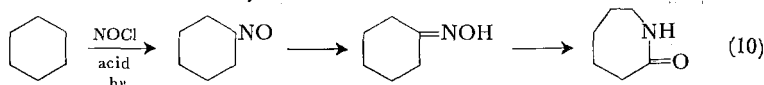
Only a few nitrosoacetylenes in which the substituent is attached to an *sp* carbon are known, none of which have been obtained in reactions employing nitric oxide. Experiments with bromoacetylene and nitric oxide led to the conclusion that the ethynyl radical ( $\text{HC}\equiv\text{C}\cdot \leftrightarrow \text{H}\dot{\text{C}}=\text{C}:$ ) is unreactive toward nitric oxide<sup>19</sup>. Primary products formed are carbon monoxide and cyanogen bromide. An indication that radicals at *sp* carbon will react with nitric oxide is found in the formation of nitrosyl cyanide on flash photolysis of either cyanogen or cyanogen bromide in the presence of nitric oxide<sup>20</sup> (equation 9) and in the pyrolysis of mercuric cyanide in the presence of nitric oxide<sup>21</sup>.



## B. Irradiation of Nitrosyl Halide and Alkanes

Irradiation of mixtures of saturated aliphatic hydrocarbons and nitrosyl halides will also lead to the formation of corresponding nitrosoparaffins. A mixture of products may be obtained from a hydrocarbon in which hydrogen atoms are not equivalent. The dimer of nitrosocyclohexane has been obtained from cyclohexane and nitrosyl chloride upon irradiation by ultraviolet light<sup>22</sup>. When the reaction, assumed to proceed by the formation and recombination of radicals, is carried out in the presence of strong acid, such as hydrochloric or sulfuric acid or phosphorous oxychloride, the product undergoes isomerization, first to the oxime and then by a

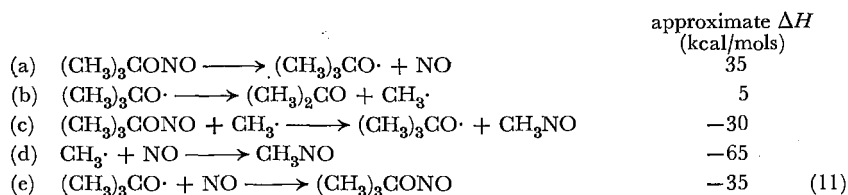
Beckman rearrangement into the cyclic amide, caprolactam<sup>23</sup> (equation 10). There is a report that irradiation of a mixture of cyclohexane, benzophenone, concentrated hydrochloric acid and nitric oxide in which oxygen is also present leads to the formation of an unidentified dinitrosocyclohexane<sup>24</sup>.



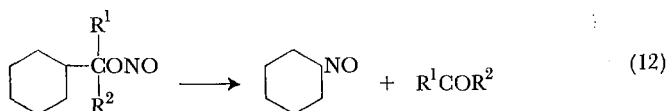
Irradiation with  $^{60}\text{Co}$  of cyclohexane solutions containing nitrosyl chloride has also brought about the formation of nitrosocyclohexane (isolated as the isomeric oxime of cyclohexanone) along with cyclohexyl chloride and cyclohexanone<sup>25</sup>.

### C. Pyrolysis and Photolysis of Nitrite Esters

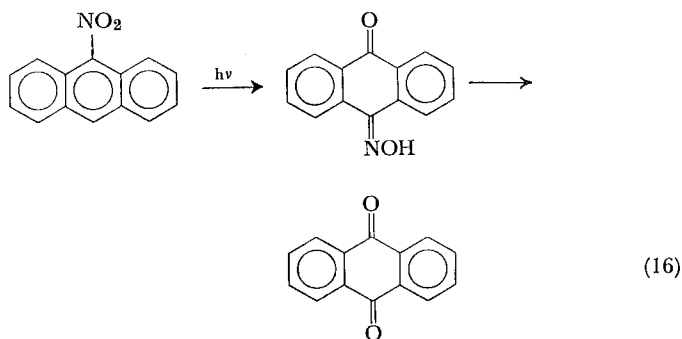
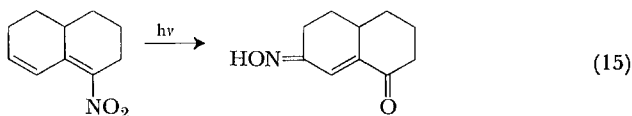
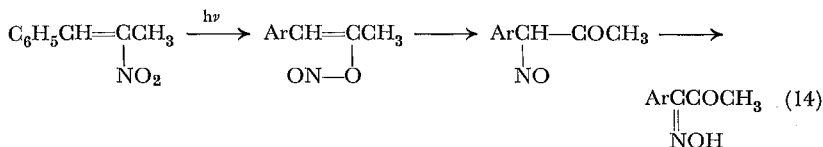
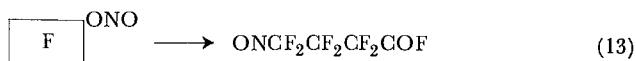
Pyrolysis or photolysis of a nitrite ester may result in an intramolecular rearrangement by a concerted mechanism or may require a dissociation followed by a recombination. The formation of nitrosomethane and acetone from *tert*-butyl nitrite by either pyrolysis<sup>26</sup> or photolysis<sup>27</sup> is satisfactorily accounted for on the basis of initial cleavage into nitric oxide and the trimethylmethoxy radical. The latter then further dissociates into acetone and the methyl radical which combines with nitric oxide (equation 11). Ethane is also produced and its formation supports the intermediacy of methyl



radicals. That alkyl radicals may react with nitrites, step (c), is demonstrated in the formation of nitrosomethane from either butyl or amyl nitrite and acetyl peroxide in which the latter must serve as the precursor of the methyl group<sup>28</sup>. One of the many preparations for nitrosocyclohexane is based on a similar reaction and demonstrates the expected tendency for the largest of the three alkyl groups which may migrate to become attached to nitrogen<sup>29</sup> (equation 12)

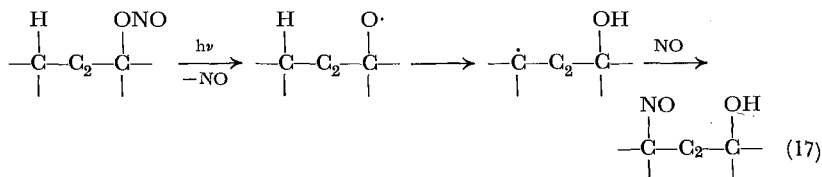


The pyrolytic ring-opening of perfluorocyclobutyl nitrite has been explained on the basis of initial dissociation into radicals but with the recognition that the reaction could proceed with ionic intermediates or could require an intramolecular concerted mechanism<sup>30</sup> (equation 13). In general cycloalkyl nitrites (ring size of 4 to 7 atoms) photolyse into  $\omega$ -nitroso aldehydes<sup>31</sup>. A similar rearrangement of a suggested intermediate vinyl nitrite has been postulated to account for the photolytic isomerization of 1-phenyl-2-nitropropene<sup>32</sup> (equation 14). A photolytic isomerization of certain nitrobutadienes and aromatic compounds may require a 1,5-migration of the nitroso group<sup>32</sup> (equations 15–16) from oxygen to carbon.



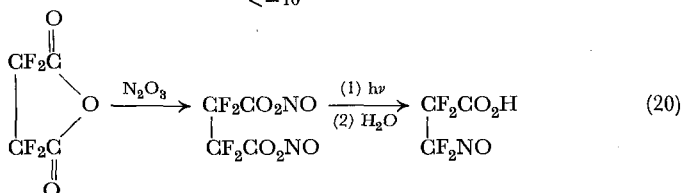
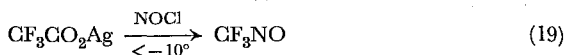
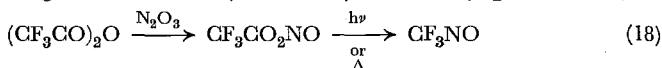
A 1,5-migration of the nitroso group from oxygen to carbon is a characteristic feature of the Barton reaction, in which alkyl nitrites (with a carbon chain of at least four atoms) may be transformed into 4-nitroso alcohols<sup>33,34</sup>. Evidently a rearrangement of an intermediate

alkoxy radical is required<sup>33,35</sup> (equation 17). It has provided a

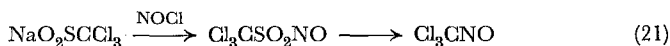


dramatic synthesis for a number of organic molecules otherwise available only with difficulty. Cycloheptyl nitrite undergoes photolytic isomerization into both 7-nitrosoheptanal and 4-nitrosocycloheptanol<sup>31</sup> but cyclooctyl nitrite gives only the Barton product, 4-nitrosocyclooctanol<sup>31</sup>.

A perfluoro acyl nitrite is available from either the corresponding acid anhydride or silver salt of the carboxylic acid. Trifluoronitrosomethane can be obtained in yields better than fifty percent from the pyrolysis or the photolysis of trifluoroacetyl nitrite<sup>36</sup> (equation 18). It has also been prepared from silver trifluoroacetate and nitrosyl chloride<sup>37</sup> (equation 19). Each reaction has been extended to perfluoro homologs<sup>38,39</sup> and to cyclic anhydrides<sup>39</sup> (equation 20).



With or without irradiation nitrosyl chloride reacted explosively with silver trichloroacetate and no product could be identified<sup>40</sup>. A successful reaction led to the formation of trichloronitrosomethane from the treatment of the sodium salt of trichlorosulfinate with nitrosyl chloride in a sealed tube<sup>40</sup> at 0° (equation 21).

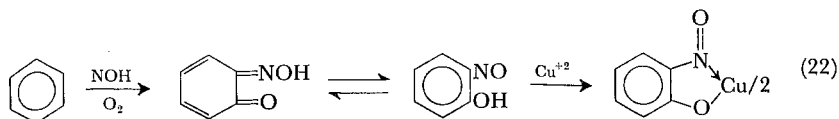


#### D. Oxidative Nitrosation (Baudisch Reaction)

According to Baudisch, oxidative nitrosation of aromatic compounds proceeds by the simultaneous introduction of the nitroso and

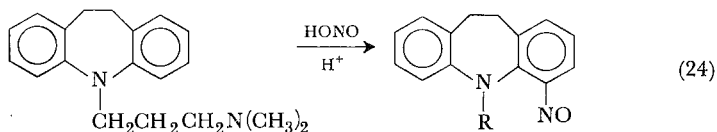
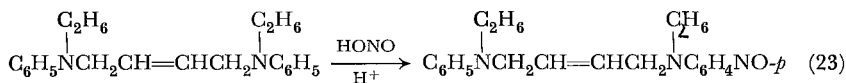


hydroxyl groups into adjacent positions on the nucleus when treated with nitrosyl hydride and oxygen. Participation of copper salts appears necessary to stabilize the nitrosyl radical and to prevent the formation of *para*-nitrosophenols<sup>41</sup> (equation 22).



### E. Nitrosation of Tertiary Aromatic Amines

Probably the first known method for nitrosation at carbon consisted in the treatment of certain aromatic tertiary amines with nitrous acid<sup>42</sup>. In this way *p*-nitroso-*N,N*-dimethylaniline is easily prepared<sup>43</sup>. A steric hindrance to the reaction may be introduced when larger groups are attached either at nitrogen or at the position *ortho* to the amino function<sup>44</sup>. Efforts to achieve dinitrosation have not been successful. Nitrosation of *N,N*-diphenylmethylamine gave only the mononitroso derivative, *p*-nitroso-*N*-phenyl-*N*-methylaniline<sup>45</sup>. Again only one benzene ring was nitrosated in experiments with *N,N*-diethyl-*N,N*-diphenyl-2-butene-1,4-diamine<sup>46</sup> (equation 23). The nitroso group is not invariably introduced into the *para*-position and sometimes an *ortho*-position is selected<sup>47</sup> (equation 24). In certain examples such as *p*-benzyl-*N,N*-dimethylaniline where



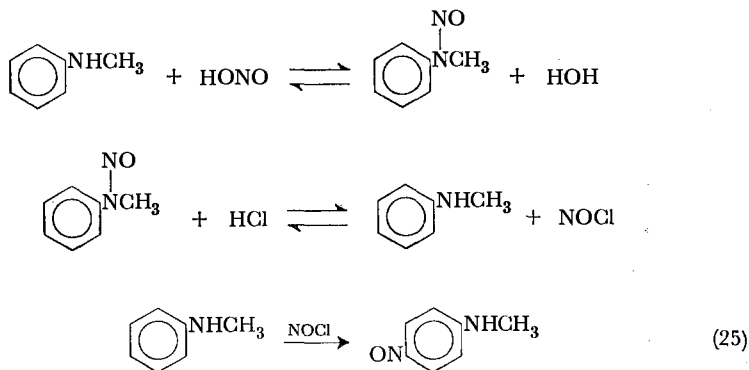
the *para*-position is already occupied, nitrosation presumably occurs *ortho* to the amine function<sup>48</sup>.

### F. Nitrosation of Secondary Aromatic Amines

#### I. Fischer-Hepp reaction

Nitrosation of secondary aromatic amines generally occurs initially at nitrogen and is reversible. In hydrochloric or hydrobromic

acid the *N*-nitroso compound rearranges to the *para*-nitroso isomer. The isomerization, known as the Fischer-Hepp reaction, proceeds intermolecularly with the intermediate formation of nitrosyl chloride followed by nitrosation generally at the *para*-position<sup>49</sup> (equation 25). Denitrosation of an aromatic *N*-nitrosamine appears to be more rapid in hydrochloric acid than it is in sulfuric acid<sup>50</sup>, in agreement with low yields for the isomerization step when carried out in sulfuric acid<sup>49</sup>. This suggests that nuclear nitrosation occurs directly when

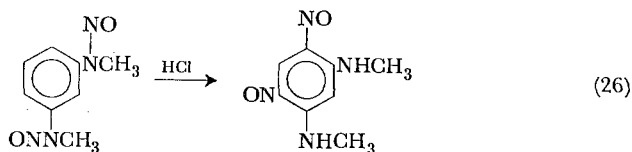


certain secondary aromatic amines are appropriately treated in concentrated sulfuric acid. The reaction does not occur in nitric acid<sup>51</sup>.

The intermediate formation of nitrosyl chloride in the Fischer-Hepp reaction was demonstrated in the formation of the nitrosyl chloride adduct of anethole when the latter was present during the treatment of *N*-nitroso-*N*-methylaniline with alcoholic hydrogen chloride in ether<sup>49</sup>.

Nitrosation in the ring may be hindered when the *para* position is occupied by another substituent<sup>49</sup> or by large substituents on the amine nitrogen<sup>51</sup>. Poor yields of *p*-nitroso *N*-*n*-hexylaniline were obtained from the *N*-nitroso isomer and the corresponding *N*-octyl analog was not transformed into its *para*-nitroso isomer<sup>51</sup>.

A particularly interesting example of the Fischer-Hepp reaction is found in the isomerization of the *N,N'*-dinitroso-*N,N'*-dimethyl derivative of *m*-phenylenediamine<sup>52</sup> (equation 26). The reaction proceeds smoothly to transform secondary *N*-nitroso- $\alpha$ -naphthyl-amines into the expected 4-nitroso isomers<sup>49</sup>; but *N*-nitroso-1-bromo-2-methylaminonaphthalene does not undergo the Fischer-Hepp reaction.

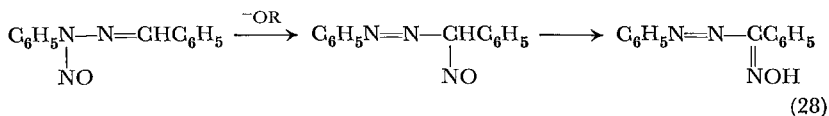


A few secondary amines have been nitrosated by nitric acid in the presence of hydrochloric acid. The addition of sodium nitrate to fuming hydrochloric acid containing *N*-ethylanthranilic acid transforms the latter into its *p*-nitroso derivative<sup>53</sup> (equation 27). From its reaction with nitric acid in alcoholic hydrogen chloride, *p*-acetamidodiphenylamine gives *p*-nitroso-*p*'-acetamidodiphenylamine<sup>54</sup>.



## 2. Base catalyzed migration

A 1,3-migration of the nitroso group from nitrogen to carbon appears to be required for an understanding of the base-catalyzed isomerization of certain *N*-nitrosohydrazones into corresponding oximes<sup>55</sup> (equation 28).



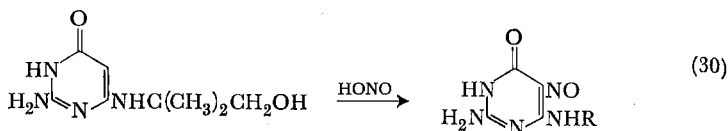
A base-catalyzed 1,2-migration of the nitroso group from nitrogen to carbon was recently discovered<sup>56</sup> (equation 29).



## G. Nitrosation of Primary Aromatic amines

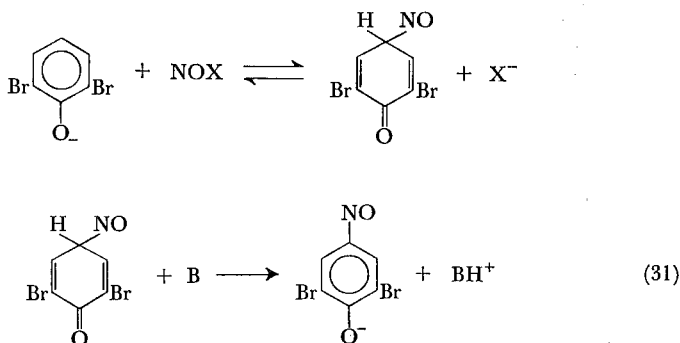
Under appropriate conditions a variety of primary aromatic amines will undergo nuclear nitrosation rather than diazotization.

Nitrosyl sulfuric acid in concentrated sulfuric acid transforms  $\alpha$ -naphthylamine into its 4-nitroso derivative<sup>57</sup> and nitrous acid nitrosates a pyrimidine ring carbon in the presence of both a primary and secondary amine function<sup>58</sup> (equation 30). In a similar reaction nitrosation occurs at the 3-position in 2-hydroxy-4-aminopyridine<sup>59</sup>.



### H. Nitrosation of Phenols

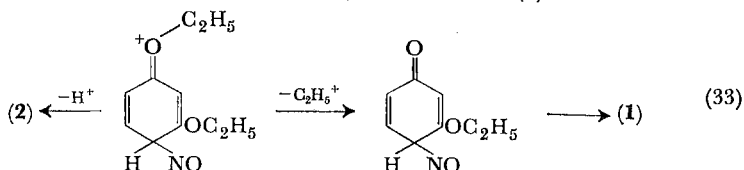
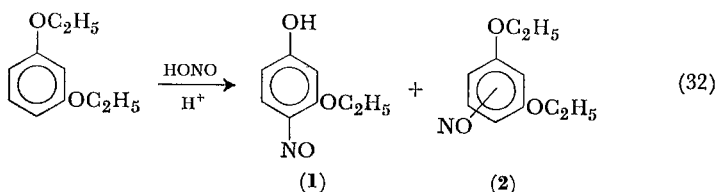
Phenols are readily nitrosated at *o*- and *p*-positions; thymol and  $\beta$ -naphthol undergo mononitrosation<sup>60</sup>. Both 2,6-dibromophenol and 2,6-dibromophenol-4-D react with sodium nitrite in aqueous alcohol by general base catalysis<sup>61</sup> (equation 31) with nitrosodeprotonation occurring faster than nitrosodeuteriation ( $k\text{H}/k\text{D} = 3.6$ ). With nitrous acid, resorcinol is dinitrosated to 2,4-dinitrosoresorcinol and phlorogucinol to trinitrosophloroglucinol<sup>62</sup>.



### I. Nitrosation of Aromatic Ethers

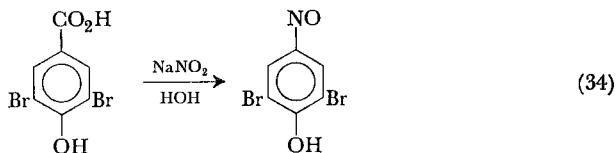
Nitrosation of aromatic ethers is virtually unknown. In mineral acid containing an alkyl nitrite, resorcinol diethyl ether is partially transformed into a nitroso derivative of the diether<sup>63</sup> (equation 32). With the assumption that the unassigned nitroso group is at the 4-position in nitrosodiethylresorcinol (**2**), the observed products are

satisfactorily accounted for by the expected intermediates (equation 33).

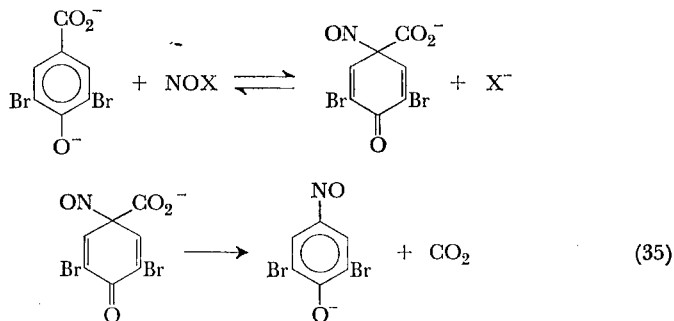


### J. Nitrosative Decarboxylation

Nitrosation by displacement of substituents is rarely found. An interesting example has come to be known as nitrosodecarboxylation<sup>64</sup>. On adding sodium nitrite to an aqueous alcoholic solution of 3,5-dibromo-4-hydroxybenzoic acid there is an immediate evolution of carbon dioxide. From the reaction, 3,5-dibromo-4-hydroxynitrosobenzene is isolated quantitatively<sup>64</sup> (equation 34).

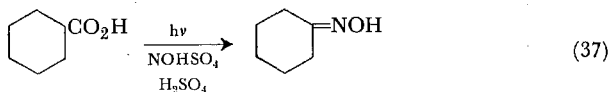
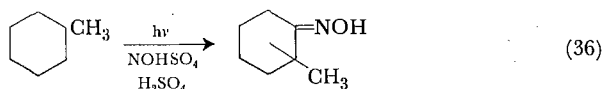


The kinetics of the reaction and comparison with bromodecarboxylation and bromodesulfonation are in agreement with the following mechanism<sup>61</sup> (equation 35). It is significant to note that

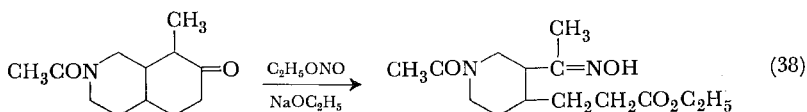


*p*-hydroxybenzoic acid nitrosodecarboxylates at least 300 times more rapidly than does *p*-methoxybenzoic acid<sup>61</sup>. Salicylic acid and its 3-, 4- and 5-methyl derivatives undergo this reaction but 3- and 5-nitro and 3,5-dinitrosalicylic acid do not<sup>64</sup>.

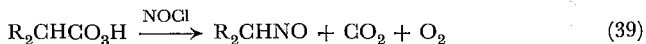
Following the observation that an attached methyl group decreased, whereas an attached carboxyl group increased, the reactivity of a tertiary carbon in a cyclohexane ring toward nitrosation by nitrosyl sulfuric acid in concentrated sulfuric acid<sup>65</sup> (equations 36, 37) it was found that cycloalkyl (ring size 5 through 7) carboxylic acids and the  $\alpha$ -branched carboxylic acids generally decarboxylated on similar treatment<sup>66</sup>. The assumption that  $\alpha$ -nitrosocarboxylic acids are intermediates<sup>67</sup> has been challenged and it is claimed that  $\alpha$ -nitrosocyclohexanecarboxylic acid is not an intermediate in the nitrosative decarboxylation of cyclohexanecarboxylic acid with the formation of caprolactam<sup>68</sup>.



The carboxyl group may be replaced by other carbonyl groups, e.g. cyclododecanone oxime is obtained from formylcyclododecane<sup>69</sup> and cyclohexanone oxime is obtained from benzoylcyclohexane<sup>70</sup>. These latter reactions are reminiscent of the base catalyzed nitrosation and cleavage of certain cyclic ketones<sup>71</sup> (equation 38). Another

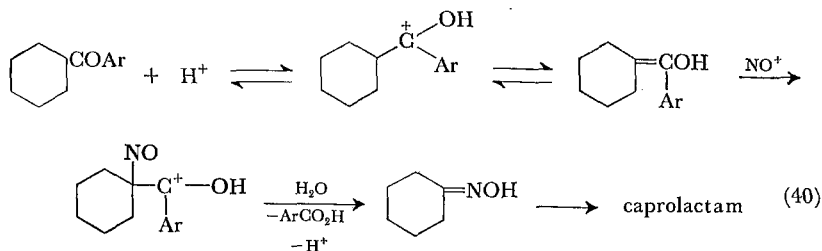


related reaction occurs when nitrosyl chloride transforms  $\alpha$ -branched peroxydicarboxylic acids into nitroso compounds<sup>72</sup> (equation 39).



Kinetic data for the reaction of aromatic ketones with nitrous acid in sulfuric acid is satisfied by a mechanism which involves the rate-determining step of deprotonation from the protonated ketone,

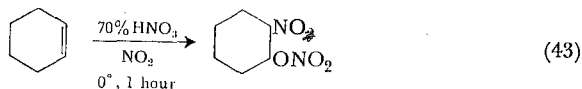
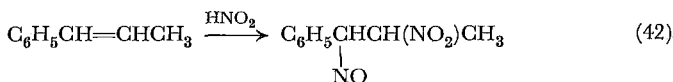
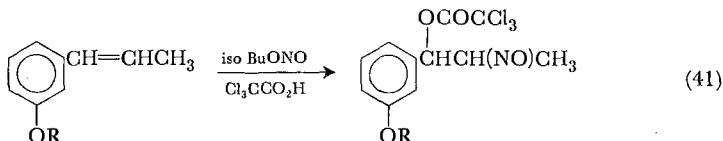
followed by a rapid nitrosation and solvolysis<sup>73</sup> (equation 40) (cf. equation 62). This may be followed by tautomerization to an oxime and a Beckmann rearrangement. When the reaction is carried out with *p*-tolylcyclohexyl ketone and nitrosyl chloride in polyphosphoric acid, caprolactam and *p*-methylbenzoic acid are formed along with *p*-tolyl- $\alpha$ -nitrosocyclohexyl ketone<sup>74</sup>.



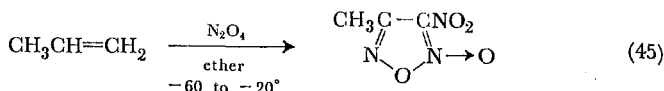
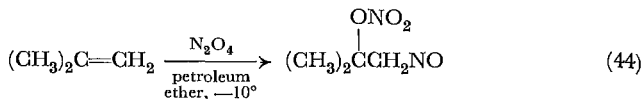
## K. Nitrosation of Olefins

### I. Nitrous acid, nitrites, nitrogen oxides and nitrosamines

Other olefins may undergo nitrosation by a related mechanism cf. equation 40. In trichloroacetic acid, certain ring-substituted derivatives of propenylbenzene treated with *iso*-butylnitrite are transformed into  $\beta$ -nitrosotrichloroacetates<sup>75</sup> (equation 41). In contrast, the treatment of propenylbenzene with nitrous acid led to the formation of the corresponding nitrosite, 1-phenyl-1-nitroso-2-nitropropane<sup>76</sup> (equation 42) and similar results have been obtained with nitrogen trioxide<sup>77</sup>. A  $\beta$ -nitroso nitrate has been prepared from cyclohexene in concentrated nitric acid and nitrogen dioxide (equation 43) and a similar reaction has been reported for the initial product from *iso*-butylene and dinitrogen tetroxide (equation 44) in the absence of weakly basic solvents such as ethers and esters which promote the

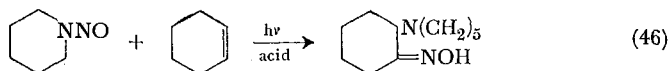


formation of nitro compound by a free radical process<sup>78</sup>. A markedly different reaction transformed propylene into 2-nitro-3-methylfuroxan when treated with dinitrogen tetroxide<sup>79</sup> (equation 45).



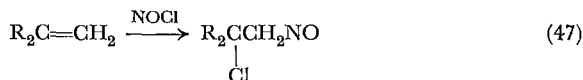
Nitrosites ( $\beta$ -nitronitroso compounds, cf., equation 42) are generally produced from olefins treated with dinitrogen trioxide ( $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$ )<sup>80</sup>. The reaction probably proceeds by a free radical mechanism initiated by an attack on an olefinic carbon by nitrogen dioxide, (cf. equation 2). Terpene nitrosites are often solid derivatives helpful in characterization.

Photochemically produced adducts of nitrosamines and olefins have been reported. The adduct from *N*-nitrosopiperidine and cyclohexene has been isolated in its tautomeric oxime form<sup>81</sup> (equation 46).



## 2. Nitrosyl halides and nitrosyl sulfuric acid

Voluminous literature on the reaction of nitrosyl halides with a great variety of hydrocarbon and fluorocarbon olefins has recently appeared. The expected adduct (equation 47) is not only often formed along with other products but also it may occur as an intermediate required for the formation of a product isolated<sup>82</sup>. Mono-

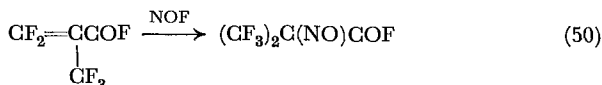
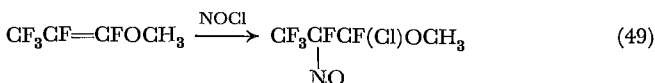
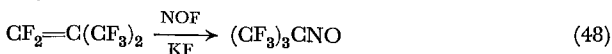


and diolefins (conjugated and unconjugated), ketene acetals, unsaturated alcohols, vinyl ethers, carbonyl compounds, nitroolefins and other hydrocarbon olefin derivatives will react with nitrosyl chloride generally under mild conditions. In certain instances, the nitroso halide may be produced *in situ* from an alkyl nitrite and hydrochloric



or hydrobromic acid. Terpene nitrosochlorides have often been made for characterization purposes.

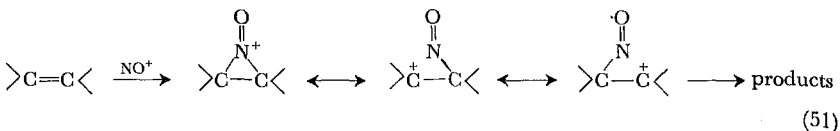
Fluorocarbon olefins also give adducts with nitrosyl halides<sup>83</sup> (equations 48, 49, 50).



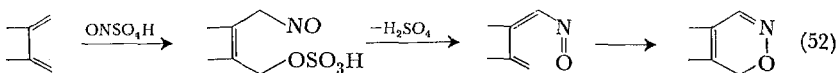
Both *cis*- and *trans*-nitrosohalide adducts of olefins may be formed<sup>84</sup>. Solvent effects on the stereochemical course of the reaction has been demonstrated in the formation of the *cis*-adduct of cyclohexene in either chloroform, methylene chloride or trichloroethylene and the *trans*-adduct in liquid sulfur dioxide<sup>85</sup>. A dependence on olefin structure has been observed in the formation of *cis*-adducts from nitrosyl chloride or bromide and norbornene in chloroform, and both *anti*-7-methoxynorbornene and norbornadiene in alcoholic acetic acid also containing hydrochloric acid<sup>84</sup>. Each reaction occurred with no molecular rearrangement. Both a four-centered cyclic transition state leading exclusively to a *cis*-adduct and a three-membered nitrosonium intermediate which might give rise to either (or both) *cis*- and *trans*-adducts have been considered<sup>84</sup>. An inter-conversion of initially formed *cis*-adducts between nitrosyl chloride and several olefins and the more stable *trans*-adduct<sup>86</sup> suggests that the addition reaction is reversible.

In a kinetic study of the addition of nitrosyl chloride to thirty different olefins in chloroform it was found that the reaction rate was influenced by both electronic and steric effects. Low activation enthalpies of 8.1 and 9.3 kcal/mole and activation entropies of -43.0 and -36.9 cal/mole<sup>-1</sup> deg<sup>-1</sup> were obtained for styrene and cyclohexene respectively. Rates for the addition to styrene and to cyclohexene increased in the solvent sequence: CH<sub>3</sub>OH < C<sub>2</sub>H<sub>5</sub>OH < CCl<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> < *n*-C<sub>7</sub>H<sub>16</sub> < C<sub>6</sub>H<sub>5</sub>Cl < C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> < C<sub>6</sub>H<sub>5</sub>CN < CH<sub>2</sub>Cl<sub>2</sub> < C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> < CHCl<sub>3</sub> and addition of Lewis acids did not accelerate the reaction<sup>87</sup>. While the evidence seems to be accommodated by a cyclic onium intermediate<sup>84</sup> (equation 51) (cf. equation 40) a free-radical mechanism has not been eliminated<sup>88</sup>; however, it would have to be initiated by a chlorine atom since it is

well established that such a reaction could not be initiated by nitric oxide (see section II.A).

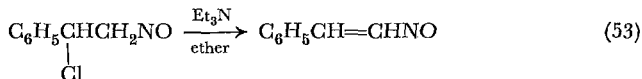


An unsaturated nitroso derivative of a bisulfate ester is formed on treatment of 2,3-dimethylbutadiene with nitrosyl sulfuric acid. Apparently the reaction is one of conjugate addition since the ester readily cyclizes with the elimination of sulfuric acid and the formation of an oxazine<sup>89</sup> (equation 52). It seems probable that the loss of sulfuric acid occurs prior to ring-closure which then may occur by valence isomerization of a presumed nitrosobutadiene intermediate.

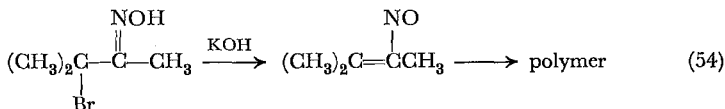


### 3. Dehydrohalogenation of olefin nitrosohalides

In the presence of base and nitrosyl chloride adducts to olefins undergo dehydrochlorination to form  $\alpha,\beta$ -unsaturated nitroso compounds. Styrene nitrosochloride with triethylamine in ether loses hydrogen chloride to form nitrostyrene<sup>90</sup> (equation 53). In similar reactions nitrosoolefins have been formed from thujene nitrosochloride<sup>91</sup> and methyl oleate nitrosochloride<sup>92</sup>.

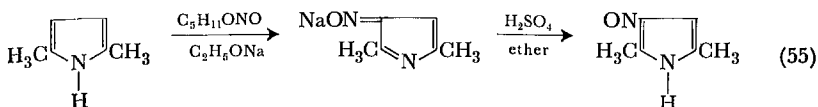


Dehydrobromination of the oxime of 3-bromo-3-methylbutanone-2 by alkali giving a polymer of 2-nitroso-3-methylbutene-2 has been claimed<sup>93</sup> (equation 54) but probably should be confirmed not only to clarify the structure of the polymer but also to elucidate the elimination mechanism insofar as initial isomerization to a nitroso compound is improbable. The reaction appears to give an example of the reversal of the conjugate addition to an  $\alpha,\beta$ -unsaturated nitroso compound (cf. III.B).

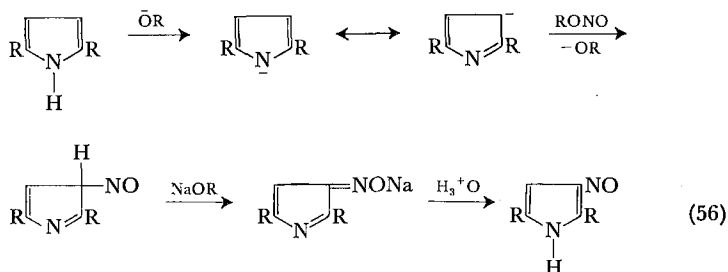


### L. Nitrosation of Phenols and Heterocycles with Nitrite Esters and Alkoxides

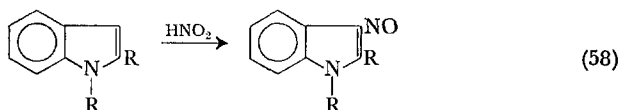
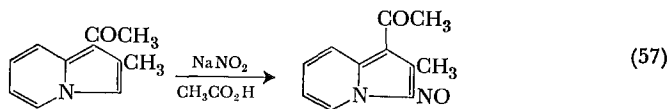
Certain phenols, e.g. resorcinol<sup>94</sup>, and aromatic heterocycles may be nitrosated by an alkyl nitrite in the presence of a metal alkoxide. From 2,5-dimethylpyrrole, treated in this manner a sodium salt may be obtained from which 3-nitroso-2,5-dimethylpyrrole may be liberated on mild treatment with acid<sup>95</sup> (equation 55). In a similar manner 3-nitrosoindoles are obtained from the corresponding



heterocycle and amyl nitrite<sup>96</sup>. Apparently these are nitrosations of heterocycle anions (equation 56). When the heterocyclic nitrogen

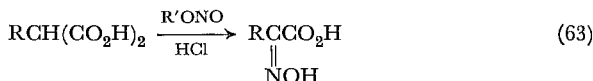
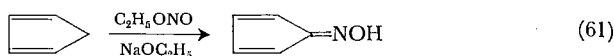
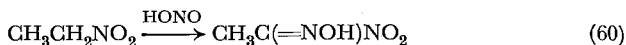
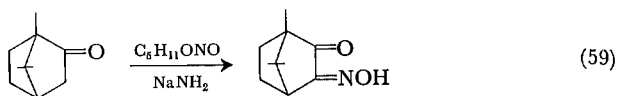


carries a substituent in place of the acidic hydrogen, nitrosation may be achieved with nitrous acid<sup>97,98</sup> (equations 57, 58).



Imidazoles with a free 4- (or 5-) position and a ring nitrogen with an attached proton may be nitrosated by amyl nitrite and sodium ethoxide in a similar manner<sup>99</sup>.

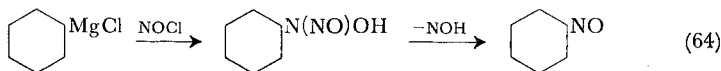
Both acid and base catalysis have promoted nitrosation at an aliphatic carbon atom with attached active hydrogen atom<sup>100</sup> (equations 59–63).



Presumably the reaction, whether acid or base catalyzed, proceeds by electrophilic attack on an  $\alpha$ -carbon atom in agreement with other condensation reactions of active methyl, methylene and methynyl groups.

### M. Organometallic Compounds and Nitrosyl Chloride

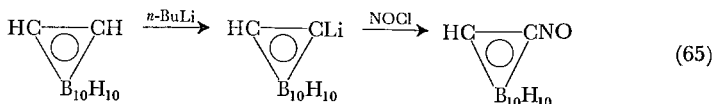
Alkylnitrosohydroxylamines<sup>101</sup> are often products from reactions between alkyl metals and nitrosyl chloride (equation 64). Nitrosohydroxylamines may lose nitrosylhydride with the formation of the corresponding nitroso compound<sup>101</sup>. Nitrosobenzene has been



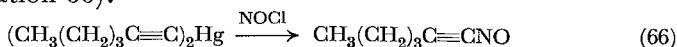
prepared by passing nitrosyl chloride into a solution of phenylmagnesium bromide<sup>104</sup> and pentamethylnitrosobenzene from the corresponding aryl mercuriacetate and ethyl nitrite in hydrochloric acid<sup>103</sup>.

Recently a nitrosocarborane has resulted from the treatment of 1-carboranyl lithium with nitrosyl chloride<sup>104</sup> (equation 65) and nitrosoalkane dimers result from the similar treatment of an aluminum trialkyl with nitrosyl chloride<sup>105</sup>. Tricyclohexylboron and

nitrosyl sulfuric acid reacted with the apparent initial formation of nitrosocyclohexane; however, products isolated represented further changes<sup>106</sup>.



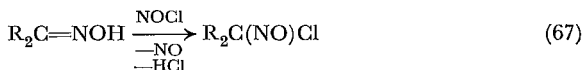
The long unknown 1-nitrosoacetylenes were first produced in a reaction in which nitrosyl chloride attacked an organo-mercury bond<sup>107</sup> (equation 66).



### N. Geminal Nitrosohalides from Oximes

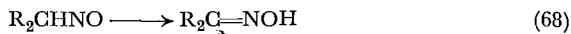
Oximes are transformed into *gem*-halonitroso derivatives on treatment with hypohalous acid. Development of the blue color of the product is the basis for Piloty's qualitative determination of the presence of an oxime<sup>108</sup>. With only occasional bursts of interest, Piloty's reaction lay dormant until *gem*-chloronitroso derivatives of hydrocarbons attracted attention as products in the reaction between irradiated nitrosyl chloride and hydrocarbons or irradiated mixtures of chlorine, nitric oxide and hydrocarbons<sup>109</sup>. The principal product is an oxime as is demonstrated in this important method for the synthesis of cyclohexanine oxime, an intermediate in a preparation of caprolactam.

Oxidation of the product to the corresponding halonitro derivative by halogens in an alkaline medium may be eliminated by treating the oxime with chlorine in ether<sup>110</sup> or by treatment with chloro-amides, e.g. *N*-chloroacetamide, *N*-chlorocaprolactam, *N*-chlorourea and *N,N*-dichlorosulfonamides<sup>111</sup>. *N*-Bromosuccinimide in aqueous sodium carbonate has also been used<sup>112</sup>. A lesser known reaction discovered by Rheinboldt<sup>113</sup> occurs between nitrosyl chloride and an oxime (equation 67) and is especially interesting in its application to aldoximes.

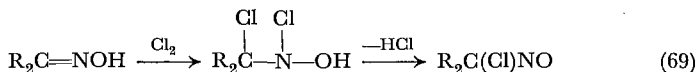


Explanations for the transformation of ketoximes into *gem*-halonitrosoalkanes on treatment with halogen have been based upon conceivable tautomers for an oxime. Halogenation of a tautomeric monofunctional primary or secondary nitrosoalkane appears to be unlikely since their prototropic rearrangement in the

gas phase, melt or in solution into oximes is not detectably reversible<sup>114</sup> (equation 68). In addition, it is reported that nitrosoparaffins are not halogenated under the conditions which transform oximes into *gem*-halonitrosoalkanes<sup>115</sup>. Addition of chlorine to the oxime

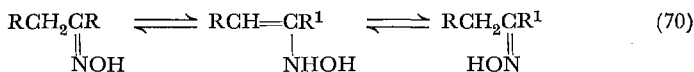


double bond followed by an elimination of hydrogen chloride (equation 69) has been accepted as more probable<sup>110</sup> but has been challenged<sup>115</sup> on the basis of an apparent requirement for hydrogen to be attached to at least one  $\alpha$ -carbon in the oxime. Of twelve

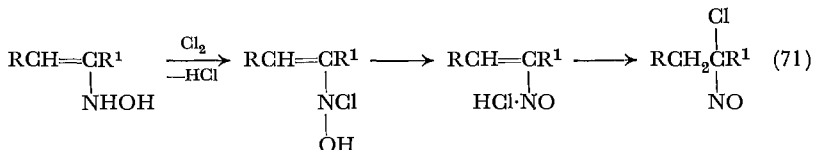


monoximes which lacked hydrogen at an  $\alpha$ -carbon, only Michler's ketone oxime reacted, as predicted, in the presence of acid, with chlorine with the formation of a nitroso compound. Although the proposed requirement for hydrogen attached to at least one  $\alpha$ -carbon was fulfilled in 75 examples of oximes which were transformed by chlorine into nitroso derivatives, it is difficult to understand why *o*- and *m*-nitroacetophenone oximes each failed to react whereas acetophenone and *p*-nitroacetophenone oximes did. Other reactions between chlorine and oximes which also contain additional reactive functional groups may occur. Benzoin oxime, for example, was not transformed into a nitroso derivative and was apparently oxidized to benzil monoxime. Nitroso compounds were not obtained from  $\alpha$ -dioximes but these are known to be transformed into furoxans under the conditions employed<sup>116</sup>.

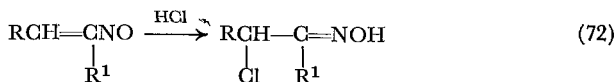
To account for the possibility of participation by hydrogen at an  $\alpha$ -carbon, Kosinski<sup>115</sup> has proposed a mechanism which invokes Raikova's tautomerization of an oxime<sup>117</sup> (equation 70). Following chlorination at nitrogen in a vinyl hydroxylamine, this mechanism



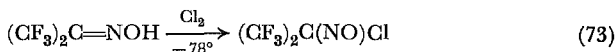
requires elimination of, followed by recombination with, hydrogen chloride<sup>115</sup> (equation 71); however, the final step in equation 71



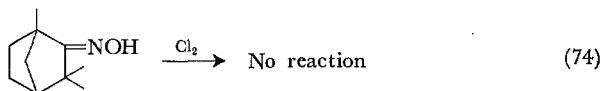
must be questioned insofar as conjugate addition of hydrogen chloride to an  $\alpha$ ,  $\beta$ -unsaturated nitrosoalkene would be expected (equation 72), cf. III.V.



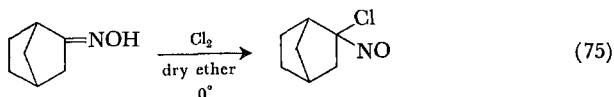
After the report that hexafluoroacetoxime reacts with chlorine at  $-78^\circ$  and is transformed into the corresponding *gem*-nitrosochloride<sup>118</sup> (equation 73), the proposed requirement for participation by hydrogen attached to an  $\alpha$ -carbon must be reevaluated. Benzophenone oxime in the presence of chlorine underwent a Beckmann rearrangement into benzanilide<sup>115</sup>.



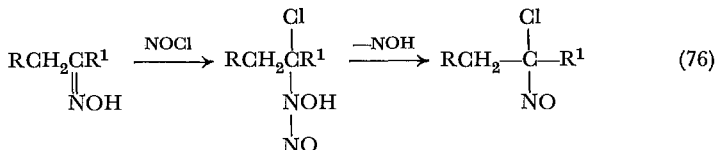
An example of an aliphatic ketoxime which does not contain hydrogen on an  $\alpha$ -carbon is found in fenchone oxime, which is unreactive toward chlorine bubbling through alkaline or neutral solutions of the oxime<sup>115</sup> (equation 74). In contrast norcamphor



oxime is transformed into the *gem*-halonitrosoderivative<sup>119</sup> (equation 75).



The reaction between nitrosyl chloride and oximes may also give *gem*-nitrosochlorides. Addition of nitrosyl chloride to the oxime linkage followed by elimination of nitrosyl hydride has been suggested<sup>120</sup> (equation 76). In support of the final step it is known that *N*-nitrosohydroxylamines reversibly dissociate into C-nitroso deriva-



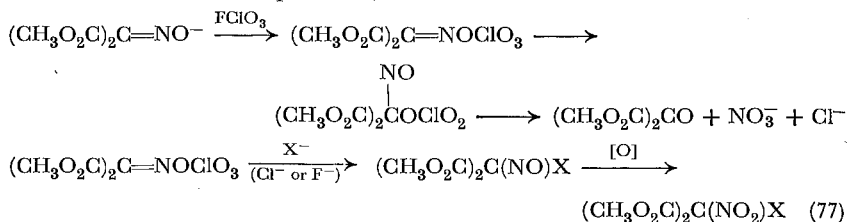
tives and nitrosyl hydride<sup>101,121</sup>. Oximes which are ordinarily unreactive to nitrosyl chloride include the oximes of benzophenone,

fluorenone, phenanthrenequinone and other ketones some of which contain hydrogen at an  $\alpha$ -carbon<sup>113</sup>.

### O. Esters of Geminal Nitrosoalcohols from Oximes

Two methods for oxidation at the  $\alpha$ -carbon of nitroso compounds are reminiscent of the reactions leading to the formation of *gem*-nitrosohaloalkanes discussed in the last section.

The intermediacy of a *gem*-nitrosofluoro derivative was assumed in the formation of dimethyl fluoronitromalonate from the reaction between potassium dimethyl oximinomalonate and perchloryl fluoride in dimethylformamide<sup>122</sup> (equation 77) and in the same reaction mixture the formation of a perchlorate ester of a *gem*-hydroxynitroso derivative is considered in an explanation for the formation of another product, a ketomalononic ester.



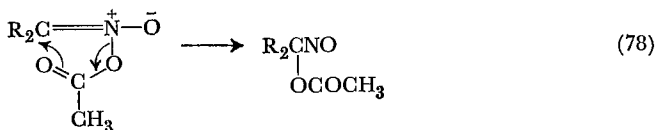
In the other oxidation, *gem*-nitrosoacetates are produced from ketoximes and lead tetraacetate<sup>123</sup> (equation 78) and oxime O-methyl ethers are reported as by-products<sup>125</sup>. Nitrosobenzoates are similarly prepared with lead tetrabenzoate<sup>124</sup>. The suggestion<sup>123,125</sup> that the reaction proceeds with the intermediate formation of free radicals has been confirmed by an esr study of comparatively stable iminoxy radicals obtained from ketoximes by oxidation with lead tetraacetate. It was concluded that the unpaired spin density resided on oxygen and nitrogen and that the structure was best described as a resonance hybrid<sup>126</sup>:  $\text{R}_2\text{C}=\ddot{\text{N}}-\ddot{\text{O}}\cdot \leftrightarrow \text{R}_2\text{C}=\dot{\text{N}}-\ddot{\text{O}}:$ . This result is consistent with initial acetoxylation at nitrogen from which either a *gem*-nitrosoacetate or an oxime O-methyl ether could be formed (equations 78 and 79). Further interaction between the *gem*-nitrosoacetate and acetoxy radicals may occur<sup>126</sup>.

For a discussion of  $\alpha$ -hydroxynitroso compounds in the Nef reaction see II.W and Chapter 7.

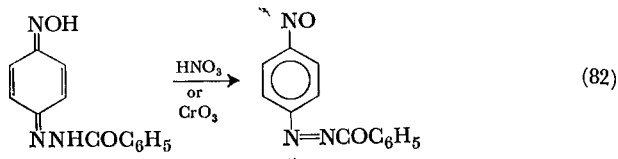
### P. Oxidation of Dioximes

Oxidation of dioximes of  $\alpha$ -diketones may lead to the formation of furoxans<sup>116</sup>. Benzil dioxime when treated with alkaline ferricyanide,



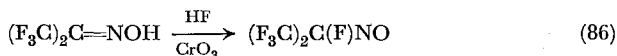
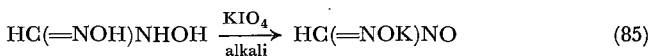
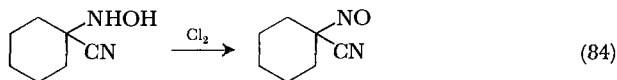
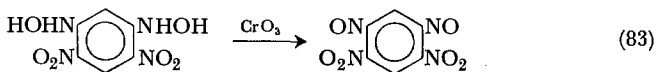


interesting analogy for the latter reaction is found in the oxidation of an oxime hydrazone derivative of *p*-benzoquinone<sup>127</sup> (equation 82).



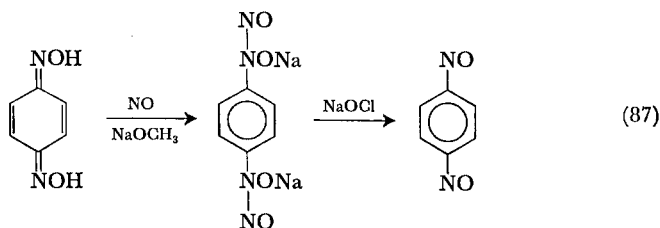
### Q. Oxidation of Hydroxylamines

Oxidation of hydroxylamines is a preferred method for the preparation of corresponding nitroso derivatives but limited in application by the accessibility of the starting materials which generally are reduction products from nitro compounds or oxidation products from primary amines. In such a two-step process nitrobenzene is reduced by zinc and ammonium chloride to phenylhydroxylamine which is oxidized by sodium dichromate in sulfuric acid to nitrosobenzene in overall yield of nearly 55%<sup>128</sup>. Other reagents which have been used to oxidize hydroxylamines include mercuric oxide<sup>129</sup>, potassium ferricyanide<sup>130</sup>, periodates in alkaline medium<sup>131</sup>, periodic acid<sup>132</sup>, chlorine<sup>133</sup>, air<sup>134</sup> and chromium trioxide<sup>135, 136</sup> (equations 83–86):



Although *N*-nitrosohydroxylamines tend to dissociate into nitroso derivatives and nitrosyl hydride<sup>101</sup>, the presence of sodium hypochlorite is advantageous<sup>137</sup> (equation 87).

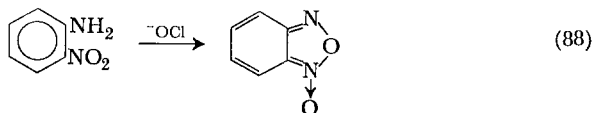
Hydroxylamines have a tendency to disproportionate into the corresponding nitroso compound and amine. After three weeks in a closed vessel, pure mesitylhydroxylamine had changed into 2,4,6-trimethylnitrosobenzene and mesidine, along with 2,4,6-trimethylnitrobenzene and azomesitylene<sup>138</sup>.



### R. Oxidation of Primary Amines

Oxidation of primary amines to hydroxylamines requires a reagent which attaches oxygen to nitrogen. Reagents which have been successful include Caro's acid (monoperoxysulfuric acid), peroxyacetic and certain other organic peroxy acids or peroxy anhydrides, hydrogen peroxide in acetic acid, permanganate (often with formaldehyde) and hypochlorous acid. Generally the subsequent oxidation occurs readily thereby providing an important route for the preparation of nitroso compounds. The elimination or suppression of further oxidation, e.g. oxidation at nitrogen to the corresponding nitro compound or oxidation at carbon, is often a limiting factor to consider.

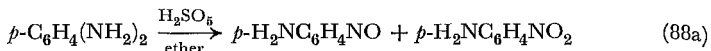
Nitrosobenzene is one of at least seven oxidation products obtained when aniline is treated with hypochlorous acid<sup>139</sup>. On the other hand, the oxidation of *o*-nitroaniline by a hypochlorite solution is a preferred method for the preparation of benzofuroxan<sup>116</sup> (equation 88). An improved yield of nitrosobenzene is reported for the oxida-



tion of aniline by permanganate with formaldehyde in sulfuric acid<sup>140</sup>, a method which transforms cyclohexylamine into nitrosocyclohexane in yields over 80 %<sup>141</sup>. The latter oxidation is also effected by hydrogen peroxide in the presence of sodium tungstate<sup>142</sup>.

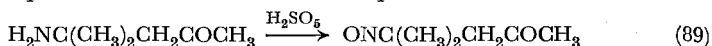
Bamberger found Caro's acid to be a general reagent for oxidizing aliphatic primary amines in which the amino group is attached to a tertiary carbon atom and for primary aromatic amines<sup>143, 144</sup>. Quantitative amounts of nitroso compounds were obtained from the isomeric nitroanilines<sup>145</sup>. Apparently, the oxidation is facilitated

by electron releasing groups; *p*-phenylenediamine is transformed into *p*-nitroaniline, but *p*-nitrosoaniline may also be isolated when the reaction is carried out in ether<sup>146</sup> (equation 88a). Acylation of one

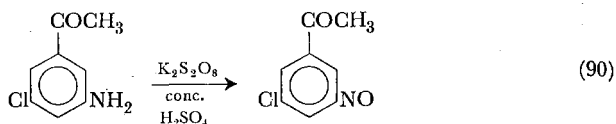


amino group controls the oxidation which proceeds to the formation of a nitroso derivative without substantial further oxidation<sup>147</sup>.

After three minutes Caro's acid in ether can oxidize *tert*-butylamine to 2-methyl-2-nitrosopropane<sup>144</sup>. Better yields are obtained in the similar oxidation of 4-amino-4-methylpentanone-2<sup>144</sup> (equation 89). The intermediate formation of nitroso compounds in the oxidation of tertiary alkyl primary amines to corresponding nitro-paraffins is demonstrated by the formation of a characteristic blue color which persists if oxidation is incomplete<sup>148</sup>.



Good yields have been reported for the oxidation of primary aromatic amines to corresponding nitroso derivatives by a peroxydisulfate in concentrated sulfuric acid<sup>149</sup> (equation 90) but perpho-

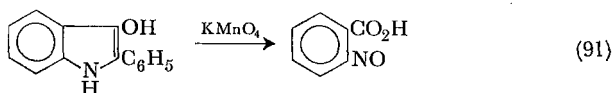


sphoric acids failed to transform certain primary aromatic amines into nitroso compounds<sup>150</sup>.

Nitrosobenzene along with phenol, diphenylamine, ammonia and nitrobenzene was a detected product following x-ray irradiation of an aqueous solution of aniline<sup>151</sup>.

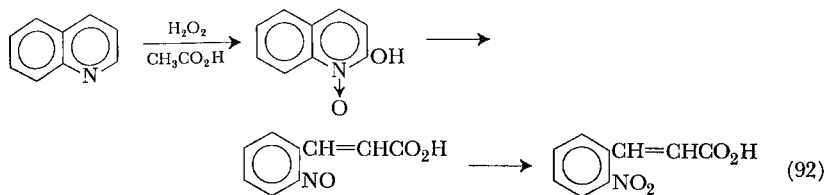
### S. Oxidation of Secondary Amines

There are a few reports of the formation of nitroso compounds from the oxidation of secondary amines. By Caro's acid, *N*-benzylaniline is transformed into nitrosobenzene, nitrobenzene, azoxybenzene and benzoic acid<sup>149</sup>. Nitrosobenzene is one of at least eight products obtained from *N*-methylaniline on treatment with Caro's acid<sup>152</sup>. Cold dilute permanganate solutions transform 2-phenyl-3-hydroxyindole into *o*-nitrosobenzoic acid<sup>153</sup> (equation 91).

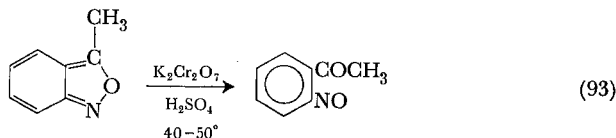


## T. Oxidation of Tertiary Amines

*o*-Nitrosocinnamic acid is a proposed intermediate in the oxidation of quinoline by hydrogen peroxide in acetic acid to *o*-nitrocinnamic acid<sup>154</sup> (equation 92). It is reported that oxidation of 3-methyl-

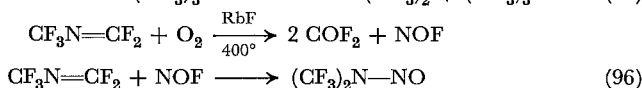
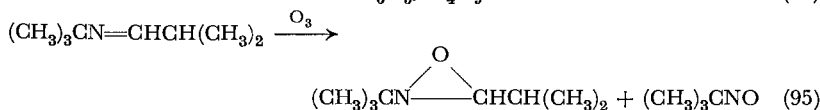
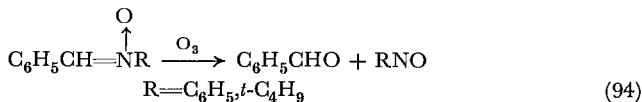


anthranil occurs with opening of the isoxazole ring and the formation of *o*-nitrosoacetophenone<sup>155</sup> (equation 93).



## U. Oxidation of Nitrones and Schiff Bases

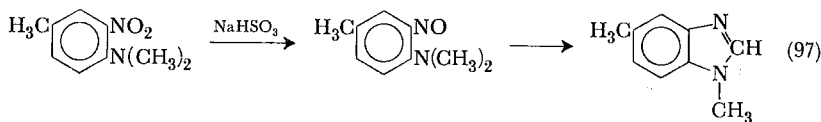
Ozonization of nitrones has produced nitroso compounds<sup>156</sup> (equation 94). Similar treatment of Schiff bases did not give nitroso products<sup>156</sup>; however the presence of a blue color during the ozonization of the Schiff base derived from *tert*-butyl amine and isobutyraldehyde has been offered as evidence for the formation of 2-nitroso-2-methylpropane<sup>157</sup> (equation 95). It was carefully established that the oxidant was ozone rather than oxygen somewhat in contrast with the catalytic oxidation of certain perfluoro Schiff bases<sup>158</sup> (equation 96) in which trifluoronitrosomethane was a considered intermediate.



## V. Reduction and Deoxygenation of Nitro Compounds

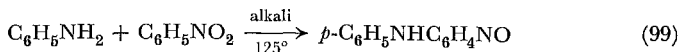
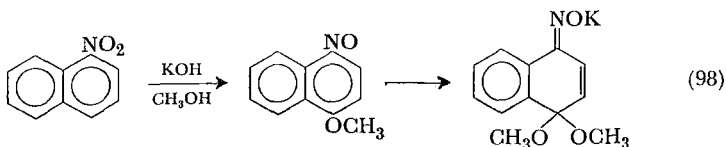
Reduction of a nitro compound leads first to the formation of a nitroso compound. In an acid medium the latter is rapidly reduced to an amine with the corresponding hydroxylamine as an intermediate. Reduction in an alkaline medium gives rise to an azoxy compound resulting from a condensation between the nitroso compound and the corresponding hydroxylamine. Best yields of nitroso compounds are generally obtained from reductions in neutral media. The exceptional reduction of primary and secondary nitroparaffins by stannous chloride does not proceed beyond the initial stage presumably because rapid isomerization to an oxime takes place.

An electrolytic reduction of nitrobenzene with a neutral electrolyte gave a good yield of nitrosobenzene<sup>159</sup>. Poor yields have been reported for deoxygenation with barium oxide<sup>160</sup> and reduction with hydroxylamine in methanol<sup>161</sup> or metallic salts such as mercuric chloride, zinc chloride<sup>162</sup> or sodium bisulfite<sup>163</sup>. In the latter example nitroso compounds are intermediates in the reductive sulfonation of aromatic nitro compounds to aminosulfonic acids (Piria reaction). With an intramolecular condensation the reduction of 3-nitro-4-dimethylaminotoluene was stopped at the nitroso stage with the formation of 1,5-dimethylbenzimidazole<sup>163</sup> (equation 97).

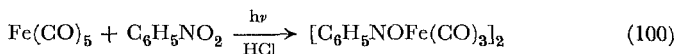


A catalytic reduction over tin of nitrobenzene to nitrosobenzene has been reported<sup>164</sup>. Over the same catalyst, nitrocyclohexane is transformed into cyclohexanone oxime.

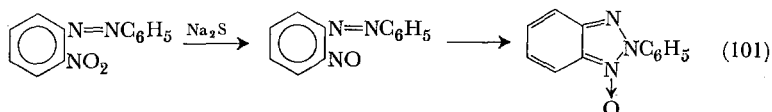
*m*-Trifluoromethylnitrobenzene is reduced to the corresponding nitroso compound by ethyl mercaptan<sup>165</sup>. Aromatic *o*- and *p*-nitronitroso derivatives are produced by treating the corresponding dinitro compounds with either hydroxylamine or stannous oxide in methyl alcoholic alkali<sup>166</sup>. The behavior of  $\alpha$ -nitronaphthalene towards alcoholic alkali is especially interesting. First one and eventually two methoxy groups become attached to the C4 position<sup>167</sup> (equation 98). Presumably a related process is required in the formation of *p*-nitrosodiphenylamine from aniline and nitrobenzene in alkali<sup>168</sup> (equation 99). A deoxygenation mechanism probably best



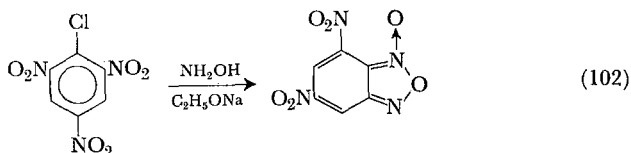
accounts for the formation of nitrosobenzene from nitrobenzene treated with iron powder in the presence of carbon dioxide at  $220^\circ$ <sup>169</sup>. Similar deoxygenations have been carried out in dry organic solvents with sodium, potassium, calcium, barium, magnesium, zinc and aluminum amalgam<sup>170</sup>. Deoxygenation of aromatic nitro derivatives by free radicals also leads to the formation of corresponding nitroso compounds<sup>171</sup>. Dimeric nitrosobenzene iron tricarbonyl is produced on irradiation of iron pentacarbonyl in nitrobenzene<sup>172</sup> (equation 100).



Ring-closure of an intermediate *o*-nitrosoazobenzene presumably accounts for the absence of further reduction of *o*-nitrosoazobenzene by sodium sulfide<sup>173</sup> (equation 101). A similar reason may be applied

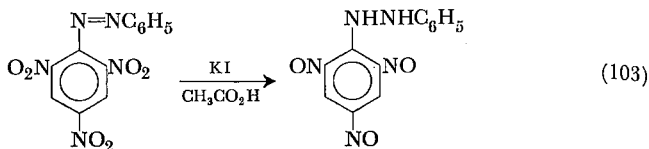


to (but is not necessarily required for) the deoxygenation of a nitro group in the transformation of picryl chloride into 4,6-dinitrobenzofuroxan by hydroxylamine in the presence of sodium ethoxide<sup>174</sup> (equation 102).

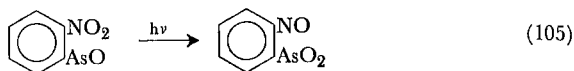
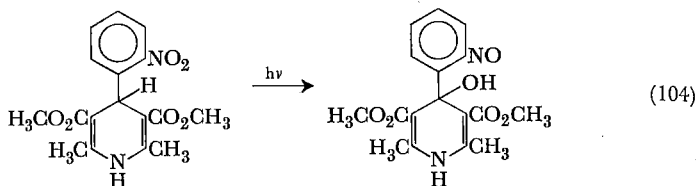


In view of the paucity of information on aromatic *m*-dinitroso-derivatives the reported formation of *N*-1,3,5-trinitrosophenyl-*N'*-phenylhydrazine from picrylazobenzene treated with potassium

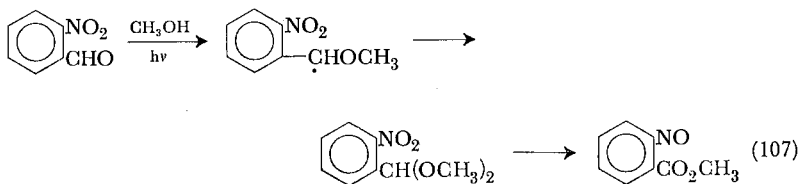
iodide in acetic acid takes on added interest<sup>175</sup> (equation 103).



By intramolecular transfer of oxygen certain nitro groups are readily deoxygenated. A classic example is found in the photochemical isomerization of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid<sup>176</sup> which takes place both in solution and in the solid state. *m*- and *p*-Nitrobenzaldehydes do not give nitroso compounds, but certain other *o*-nitro derivatives undergo similar rearrangements<sup>177,178,179</sup> (equations 104, 105, 106).

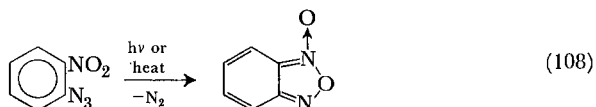


In the isomerization of *o*-nitrobenzaldehyde, the transfer of oxygen from an activated nitro group to the carbonyl carbon probably occurs by a redistribution of electrons when the nitro and aldehyde groups are coplanar with the aromatic ring<sup>180</sup>. A kinetic study by esr of free radicals produced during the reaction did not lead to a definitive explanation<sup>181</sup>. When the reaction is run in methanol, it is claimed that irradiation first brings about the formation of the dimethylacetal of *o*-nitrobenzaldehyde from an intermediate methoxy *o*-nitrobenzylradical<sup>182</sup> (equation 107). The acetal is then transformed into methyl *o*-nitrosobenzoate.

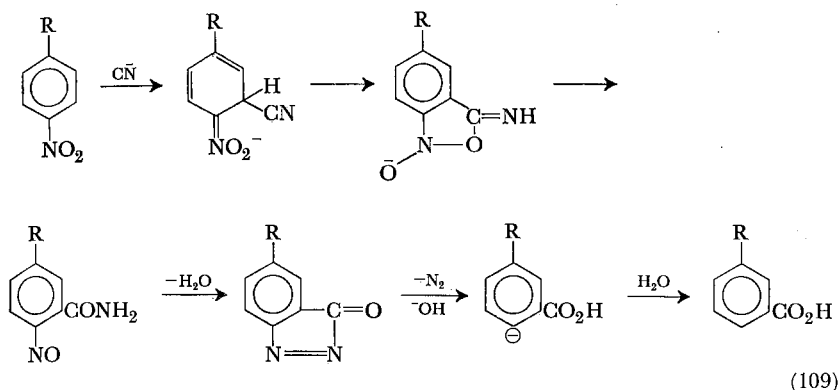




An intramolecular transfer of oxygen from the nitro group to nitrogen attached at the *ortho*-position is required in both the pyrolytic and the photolytic transformation of *o*-nitrophenyl azide into benzofuroxan<sup>116</sup> (equation 108), cf. II.P.

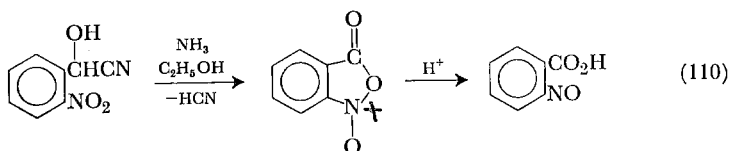


A derivative of *o*-nitrosobenzamide is a probable intermediate in the von Richter reaction whereby an aromatic nitro compound is transformed by aqueous alcohol containing an alkali cyanide into an aromatic acid in which the carboxyl group occupies a position *ortho* to the position from which the nitro group was ejected<sup>183</sup> (equation 109). *o*-Nitrosobenzamide, independently prepared, under-

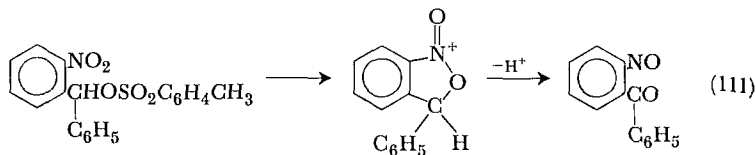


went the required reaction with both aqueous hydroxide and cyanide ions with the formation of benzoic acid<sup>184</sup>.

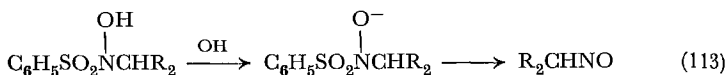
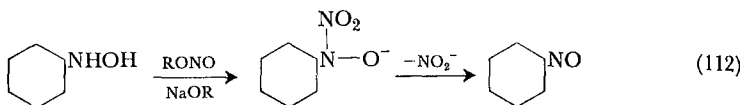
An explanation for the transformation of *o*-nitromandelonitrile by treatment with ammonia into *o*-nitrosobenzoic acid, first reported in 1906<sup>185</sup> and of *o*-nitrobenzaldehyde by treatment with potassium cyanide into the same product<sup>186</sup> may now be given an explanation similar to Rosenblum's mechanism for the von Richter reaction (equation 110). A similar reaction was found in the formation of



*o*-nitrosobenzophenone on treating 2-nitrobenzhydrol with *p*-toluenesulfonyl chloride in pyridine for which the following explanation was offered<sup>187</sup> (equation 111).

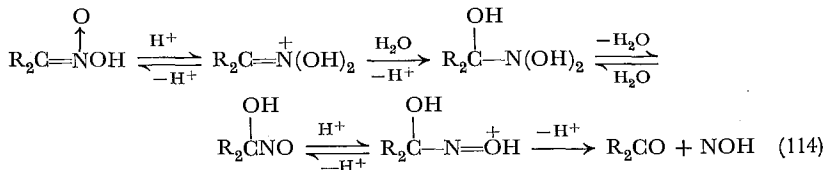


The step in which a nitroso group is generated in equations 93, 109, 110 and 111 and probably in equations 104, 106 and 107 requires opening of an isoxazoline ring, cf. II.X. When this derivative is also a cyclic hydroxamate anion<sup>108,110</sup> there is an analogy with the dissociation of linear hydroxamate anions<sup>188</sup> (equations 112, 113).

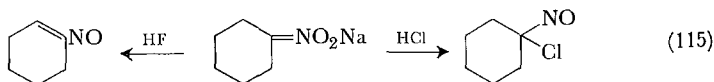


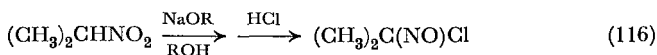
### W. Nef Reaction

Hydrolysis of *aci*-nitroalkanes, the Nef reaction, is often utilized as a preparative method for carbonyl compounds. A persistent blue color in the reaction mixture during the time that *aci*-nitroalkane is being destroyed indicates the presence of a nitroso group. A reasonable mechanism for the Nef reaction in which  $\alpha$ -hydroxynitrosoalkanes are intermediates has been proposed<sup>189,190</sup> (equation 114).

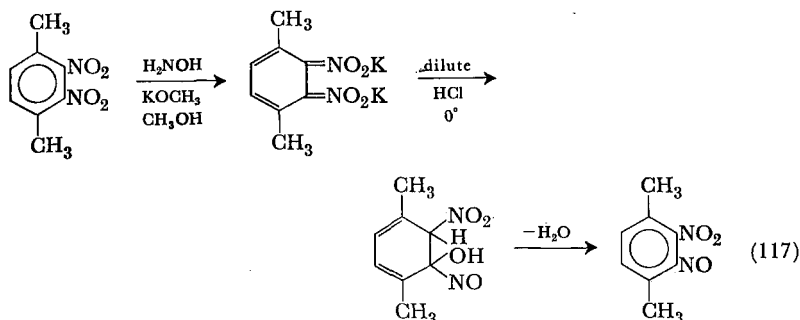


Isolation of an  $\alpha$ -hydroxynitrosoalkane has apparently not been realized; however the reaction carried out in cold hydrochloric acid has led to the formation of  $\alpha$ -chloronitrosoalkanes<sup>191</sup> (equations 115, 116).



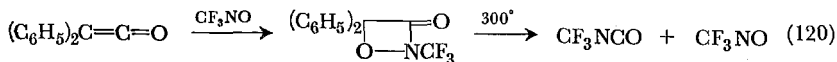
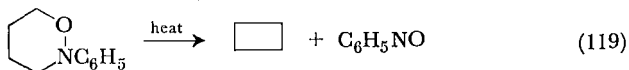
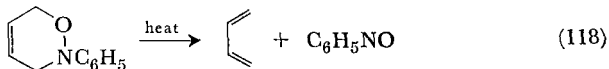


The second step in the formation of 2-nitroso-3-nitro-*p*-xylene from the corresponding dinitro compound by reduction followed by treatment with aqueous acid appears to follow the Nef reaction up to the stage of an alternative dehydration with aromatization<sup>192</sup> (equation 117).



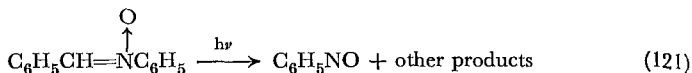
## X. Pyrolysis of Heterocycles

A few reports begin to indicate that saturated and certain partially saturated rings containing a ring oxygen adjacent to a ring nitrogen bearing an exocyclic substituent will undergo pyrolysis with the release to the corresponding nitroso compound. Both 3,6-dihydro- and tetrahydrooxazines will liberate nitroso compounds on heating<sup>193</sup> (equations 118, 119) and a similar reaction is known for a 4,4-diphenyloxazetidinone<sup>194</sup> (equation 120).

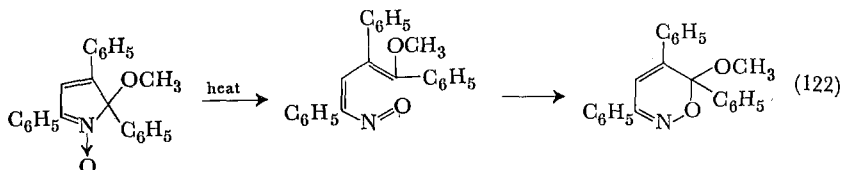


A prediction that certain five membered heterocyclic *N*-oxides would undergo pyrolytic or photolytic ring-cleavage with the formation of a nitroso compound is based on the formation of nitroso-benzene from azoxybenzene by pyrolysis<sup>195</sup> and from *N*-phenyl-benzalnitron by photolysis<sup>196</sup> (equation 121) and the ring-opening

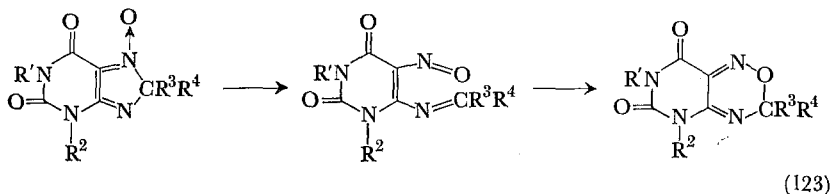
of benzfuroxan, cf. II.P. An example may have been found in the



pyrolytic transformation of 2,3,5-triphenyl-2-methoxypyrrole-*N*-oxide into the corresponding 1,2,6-oxazine<sup>197</sup>. An attractive explanation based on the principles of valence isomerization requires ring-opening to a nitrosodiene followed by a new ring-closure (equation 122), cf. II.K.2. The facile conversion of an imidazole-*N*-oxide into



an oxadiazine<sup>198</sup> (equation 123) may also proceed by valence isomerization into a nitroso compound followed by a new ring-closure.

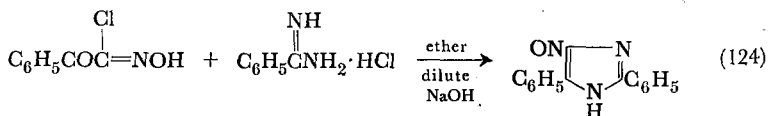


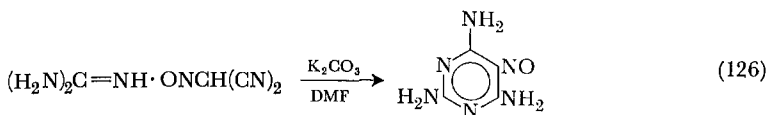
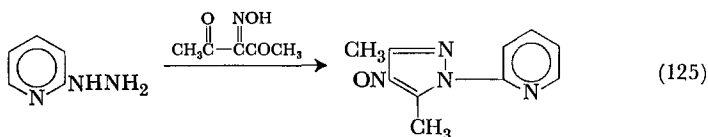
## Y. Electrolysis of oxime Salts

A report that electrolysis of a 1:1 mixture of the oxime of mesoxalic ester and its sodium salt occurs with intermolecular coupling between the two  $\alpha$ -carbon atoms and the formation of a 1,2-dinitroso derivative of an ethane<sup>199</sup> should be reinvestigated. In another report it is claimed that ketoximes undergo electrolytic oxidation in dilute sulfuric acid to give *gem*-nitronitroso compounds<sup>199</sup>.

## Z. Condensation Reactions

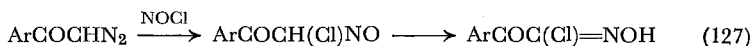
A variety of nitroso derivatives of heterocyclic aromatic compounds have been obtained by reactions in which the heterocyclic ring is produced by an intramolecular condensation. The following examples are illustrative<sup>200,201,202</sup> (equations 124, 125, 126).



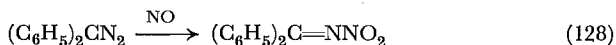


### Z<sub>1</sub>. Nitroso Compounds from Diazo and Diazonium Compounds

Derivatives of diazoacetophenone in the presence of nitrosyl chloride release nitrogen and form geminal nitrosochloride adducts<sup>203</sup> (equation 127); however, it is not established that a carbene is an intermediate. Nitric oxide reacts with diphenyldiazomethane

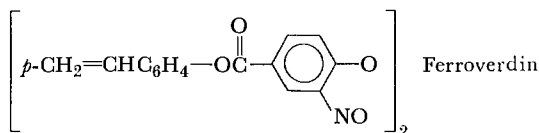


to form a nitrimine<sup>204</sup> (equation 128) presumably by way of an iminoxy radical,  $(\text{C}_6\text{H}_5)_2\text{C}=\text{NO}$ , which has been detected<sup>205</sup>. Nitrosobenzene has been prepared from the combination of phenyldiazonium chloride and an alkaline solution of potassium ferricyanide at 0° for 80 hours<sup>206</sup>.



### Z<sub>2</sub>. Natural Occurrence

Aromatic nitroso compounds have been isolated as animal metabolic intermediates from corresponding aromatic primary amines and from corresponding aromatic nitro compounds<sup>207, 208, 209</sup>. Bacterial degradation of *p*-nitrobenzoic acid to *p*-aminobenzoic acid apparently requires the intermediacy of *p*-nitrosobenzoic acid<sup>210</sup>. The green pigment ferroverdin is obtained from a species of *Streptomyces*<sup>211</sup>.



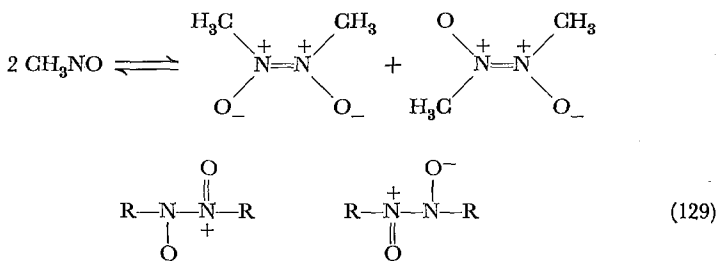
### III. STRUCTURE AND REACTIONS

#### A. Dimerization

The diamagnetism for C-nitroso compounds was first demonstrated in a measurement of the magnetic susceptibility of nitrosobenzene and its *p*-dimethylamino derivative<sup>212</sup>. Recently the first example of paramagnetic resonance absorption for a C-nitroso compound was reported for 1-acetoxy-2-methyl-2-nitrosopropane (colorless solid) in a 0.1 M solution (blue) in toluene. The solution contained about six percent of a biradical presumably derived from a dimer. An esr signal was not obtained in similar investigations on *p*-nitrosotoluene, 2-chloro-2-nitrosopropane and 1-chloro-1-nitrosocyclohexane<sup>213</sup>.

A tendency toward dimerization is a distinctive property of the nitroso group when attached to carbon. It is intimately associated with, and usually detected by the disappearance of the blue or green color which originates from an  $n \rightarrow \pi^*$  transition with weak absorption in the 6300–8300 Å range ( $\epsilon = 1$  to 60) and is characteristic of the monomer. Many, but by no means all, examples are colorless or pale yellow dimers in the solid state, becoming monomeric on melting, in the gas phase, or in solution. Two types of dimers are known; one is an *N,N'*-azodioxide, the other is an *N,N*-diperfluoroalkyl-O-nitrosohydroxylamine. There is no known example of a monomer which gives both dimers.

Nitrosomethane dimer has the structure of *cis*- and *trans*-*N,N'*-dioxoazomethane<sup>214</sup> (equation 129). Each configuration may be represented with additional resonance structures as shown. When



they will dimerize, nitroso derivatives of alkanes, alkenes, presumably alkynes, and aromatic compounds follow the pattern set by nitrosomethane and yield the expected dioxide of an azo compound. This dimer structure is well established by both chemical and physical evidence<sup>215</sup> but primarily by x-ray crystallography<sup>216</sup>.

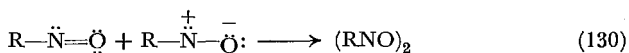
Reduction of the dimer of  $\alpha$ -nitrosotoluene to  $N,N'$ -dibenzylhydrazine by aluminum amalgam<sup>217</sup>, its acid hydrolysis into benzhydrazide<sup>218</sup> and the formation of tetrahydropyridazines from nitroso dimers and dienes (c.M) clearly demonstrate the dimer N—N bond. In general, mixed dimers are unknown; however an incompletely characterized mixed dimer from a nitrosoheptane and 4-nitroso-1-octanol has been reported<sup>219</sup>. There continues to be attempts to refine the description of the bonding and recently bond orders of  $\frac{3}{2}$  were considered for the dimer ONNO system<sup>220</sup>.

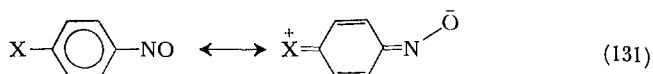
A greater thermodynamic stability by about 25 kcal/mole for nitrosoparaffin dimers with respect to corresponding monomers is diminished and monomers are stabilized when electron-withdrawing groups are attached at the  $\alpha$ -position<sup>221</sup>, e.g. the blue monomer, 2-bromo-2-nitrosopropane, gives no indication of dimerization<sup>222</sup>.

Monomers of nitrosoaromatic derivatives may be stabilized by resonance. Presumably this accounts for the dissociation of nitrosobenzene dimer in benzene occurring too rapidly to be measured<sup>222</sup>. Conjugation between an electron releasing substituent in the *para*-position and the nitroso group further enhances the stability of the monomeric form of nitrosobenzene with respect to its dimer<sup>223,224</sup>. This effect is most pronounced in *p*-dimethylamino- and *p*-iodo-nitrosobenzene which are blue solid monomers<sup>223</sup> and in *p*-nitroso-anisole<sup>225</sup> and *p*-bromonitrosobenzene<sup>223</sup> which are blue solid monomers under some conditions.

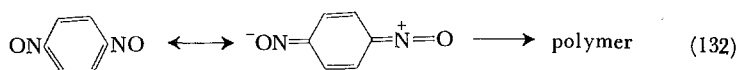
Stabilization of the dimeric form relative to monomeric derivatives of nitrosobenzene is brought about by *ortho*-substitution and is most pronounced when both *ortho*-positions are occupied by groups larger than hydrogen. A spectrophotometric study of the monomer-dimer equilibrium in benzene for a series of derivatives of 2,6-dichloronitrosobenzene demonstrated that an electron releasing substituent at the 4-position favors dissociation to the monomer. That dimer dissociation is electron-demanding was indicated by a  $\rho$  value of  $-1.5$ , obtained in the usual Hammett  $\rho\sigma$  treatment. A change in  $\Delta F^\circ$  gave a measure of the 'resonance effect' of the 4-substituents ( $\text{CO}_2\text{C}_2\text{H}_5$ , H,  $\text{CH}_3$ , Cl, Br and  $\text{OCH}_3$ ) which was found to be identical with the isoelectronic derivatives of benzaldehyde as determined from the reversible formation of derivatives of benzaldehyde cyanohydrin<sup>224</sup>.

A postulated dimerization by an ionic reaction<sup>223</sup> (equation 130) is in agreement with the resonance structures (equation 131) in

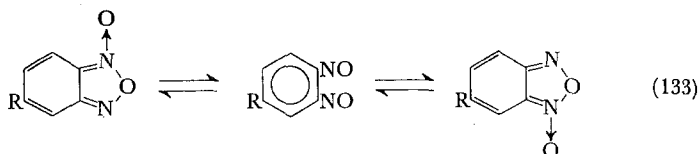




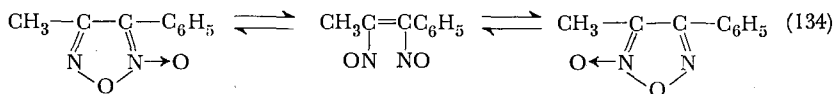
which the nitroso group is electron withdrawing. The *ortho*- effect may be attributed to steric inhibition of resonance in the monomer<sup>226</sup> or to a stabilization of the dimer through steric inhibition of resonance resulting in a stronger N—N bond (more nearly a double bond)<sup>215, 227</sup>. In contrast with *p*-nitronitrosobenzene which is a pale yellow solid dimer, *p*-dinitrosobenzene when freshly sublimed is a green solid monomer. It rapidly changes to a pale yellow polymer<sup>228</sup> (equation 132).



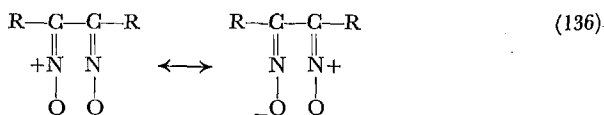
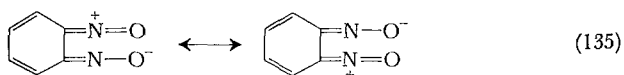
Dimerization may be eliminated if intramolecular interaction between the nitroso group and an *o*-substituent in an aromatic compound may occur. *o*-Dinitrosobenzene has been a postulated intermediate<sup>229</sup> in the equilibration of unsymmetrically substituted benzfuroxans<sup>230</sup> (equation 133). A dimer of *o*-dinitrosobenzene is unknown. In a very similar equilibrium, dinitrosoolefins are assumed



intermediates in the pyrolytic isomerization of unsymmetrically substituted monocyclic furoxans<sup>203</sup> (equation 134). In each example (equations 133, 134) the intermediate may exist as zwitterionic

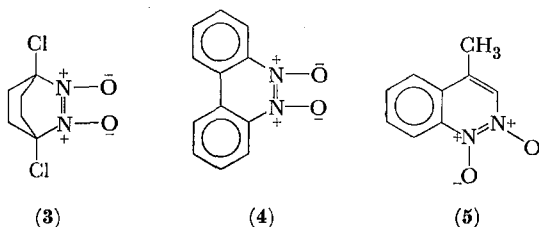


resonance structures (equations 135, 136).





In general dimers of nitrosoalkanes are more stable in the *trans*-configuration<sup>214</sup>. Certain cyclic azo-*N,N'*-dioxides are allowed only in the *cis*-configuration, e.g. the azodioxides (**3**, **4**, **5**) from ring-closure of 1,4-dichloro-1,4-dinitrosocyclohexane<sup>116</sup>, 2,2'-dinitrosobiphenyl<sup>116</sup> and 4-methylcinnoline-1,2-dioxide<sup>231</sup>. Dissociation of the 'internal nitroso dimers' which are also cinnoline dioxides has not been demonstrated, in contrast with the ring-opening of furoxans, *vide supra*.

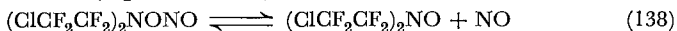


Nitrosobenzene dimer exists in the *cis*-configuration but its *p*-bromo derivative is a *trans*-dimer. Apparently an example of a dimer of a nitrosoaromatic compound in both *cis*- and *trans*-configurations has not been reported<sup>231</sup>. Conversion of a *trans*-nitrosoalkane dimer to the *cis*-isomer may be brought about by ultraviolet irradiation; the reverse process occurs readily in nonpolar solvents without irradiation<sup>214</sup>. Similarities in solvent effects for both the conversion of *cis*- to *trans*-dimers and the dissociation of dimers suggests the intermediacy of the corresponding monomers in dimer isomerization.

The other known mode of dimerization is a photochemical reversible reaction and may be illustrated with trifluoronitroso-methane<sup>232</sup> (equation 137). This is discussed in detail in Chapter 4.



A dimer of  $\beta$ -chlorotetrafluoronitrosoethane has been obtained from the combination of nitric oxide and the stable di- $\beta$ -chlorotetrafluoroethyl nitric oxide<sup>233</sup> (equation 138).



## B. Isomerization to Oximes

The nitrosation of aliphatic carbon atoms is an important preparative method for oximes (isonitroso compounds in the older literature) in which the intermediate nitroso derivative may or may not be isolated. Isomerization to the oxime, in the gas phase, with melting or in a solution, may occur more rapidly than dimerization,

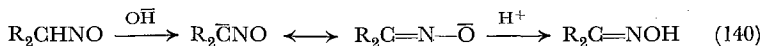
and is catalyzed by polar solvents, strong acids and bases and nitric oxide<sup>231</sup>. It is apparently irreversible (equation 139). When the nitrosating agent is nitrous fumes ( $\text{N}_2\text{O}_3$ ) and the reaction is carried



out in ether, the intermediate nitroso compound may be isolated<sup>234</sup>. The first-order vapor phase isomerization of nitrosomethane, complicated by a contribution from a surface reaction, apparently proceeds by an intramolecular hydrogen transfer in agreement with a high negative entropy of activation<sup>235</sup>.

As the molecular weight increases, the rate of isomerization may decrease as is seen in the increasing resistance toward isomerization for  $\text{RNO}$  in the series  $\text{R} = \text{CH}_3$ ,  $\text{CH}_2\text{CH}_3$ ,  $\text{CH}(\text{CH}_3)_2$ ,  $\text{C}(\text{CH}_3)_3$ .<sup>5</sup> A particular interest may be found in  $\alpha$ -nitrosotoluene which partially isomerizes into benzaldoxime on formation by the oxidation of benzylhydroxylamine with dichromate but is predominantly transformed into an extraordinarily stable nitroso dimer<sup>218, 236</sup>. When treated with hydrogen chloride in chloroform it is converted to a mixture of benzhydrazide and its benzyldene derivative, both of which have retained linked nitrogen atoms<sup>218</sup>. Based on this information, it would appear probable that the conversion of certain nitrosoalkane dimers into corresponding oximes requires the intermediacy of the monomer. This is in agreement with the rearrangement of secondary nitroso dimers in the presence of hydrogen chloride which is dependent only on dimer concentration suggesting that the rate-determining step is likely to be dissociation to monomer<sup>237</sup>.

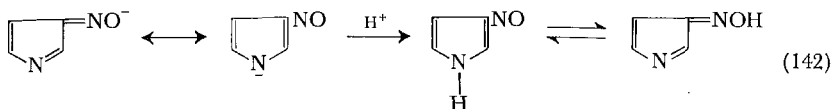
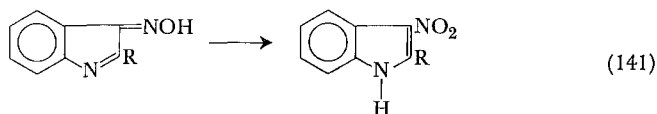
It may be assumed that the base catalyzed isomerization of a nitroso monomer to the corresponding oxime proceeds by the initial abstraction of a proton from the  $\alpha$ -carbon atom. It would then appear that the resulting carbanion exists in resonance with an oximino anion (equation 140); however, available chemical evidence indicates that this anion reacts with cations only at oxygen and/or



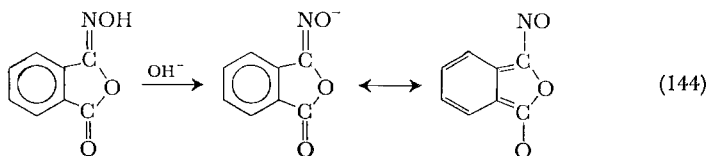
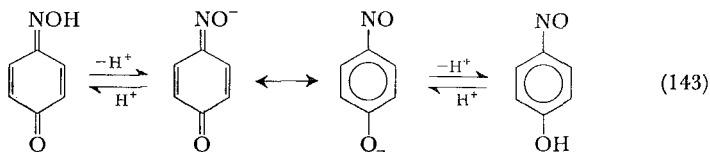
nitrogen. An analogous resonance structure for the iminoxy radical ( $\text{II.O}$ ), in which the unpaired spin density resides on oxygen and nitrogen and not on carbon, has been described. This problem of electron density distribution may be extended to the interesting nitrosolate anions,  $\text{R}-\text{C}=\text{NO}^-$ . Available information does not



answer either the questions on the equivalence of the nitrogen atoms and of the oxygen atoms or the question of alkylation at carbon. Apparently *gem*-dinitroso compounds of the type  $R_2C(NO)_2$  where  $R \neq H$  are not known. A striking example of oxime stability with respect to its nitroso isomer is found in an indolone oxime. Its reactions, e.g. permanganate oxidation to the corresponding 3-nitroindole, do not require the intermediacy of a nitroso isomer (equation 141). Indeed 3-nitrosoindoles are unknown except in certain examples where the ring nitrogen carries a substituent.  $\beta$ -Nitrosopyrroles give a fleeting green color on liberation from their salts but rapidly change to yellow, presumably indicative of the isomeric oximinopyrrolenine structure<sup>238</sup> (equation 142).

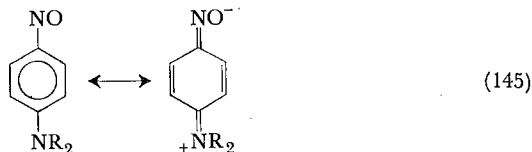


An equilibrium between *o*- and *p*-nitrosophenol with the respective quinone monoxime is well established. In solutions, *p*-nitrosophenol (about 15%) and *p*-benzoquinone monoxime (about 85%) are detected by analysis of spectroscopic data<sup>239</sup> (equation 143). The isomers are isolated in two crystalline forms, one is pale green, the other is colorless. Alkaline solutions give a reddish-green color. A similar bright red anion was obtained from the oxime of phthalic anhydride<sup>240</sup> (equation 144).

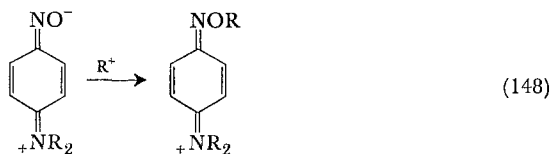
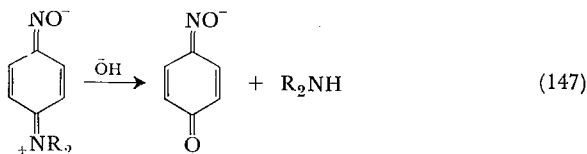
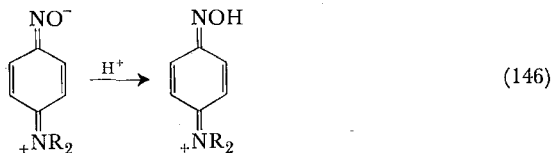


### C. Nitrosoaromatic Amine Zwitterions

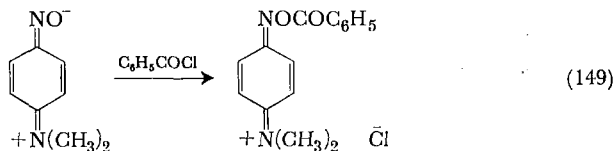
A contribution from a resonance zwitterionic structure assigned to primary, secondary and tertiary *p*-aminonitrosobenzene derivatives (equation 145) is reminiscent of a similar expression for *p*-dinitrosobenzene, cf. III.A. It readily provides a basis for explaining



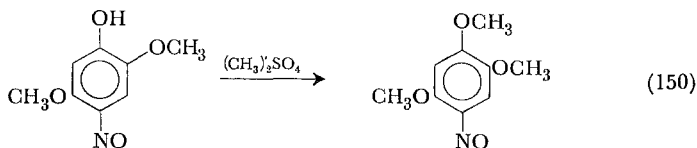
reactions with acids and bases and alkylations (equations 146, 147, 148) and accounts for the high dipole moment of *p*-nitrosodimethylaniline<sup>218</sup>. Alkylation (equation 148) occurs at oxygen rather than



at amine nitrogen (see equation 145) as is seen from the product which on hydrolysis gives a dialkyl- rather than a trialkylamine<sup>241</sup>. It has been reported that acylation also occurs at oxygen<sup>242</sup> (equation 149).

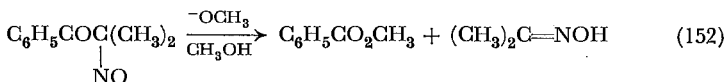
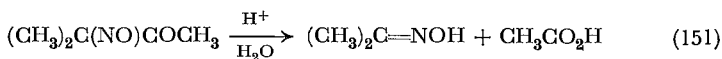


In contrast nitrosophenols may alkylate at the phenolic oxygen as is seen in the formation of 2,4,5-trimethoxynitrosobenzene from 2,5-dimethoxy-4-hydroxynitrosobenzene and dimethyl sulfate<sup>243</sup> (equation 150).

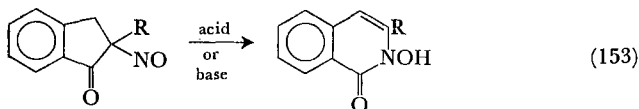


#### D. Activation of Other Substituents

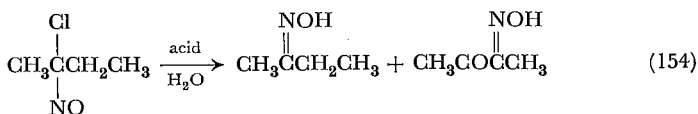
A substituent other than hydrogen may be labile at the  $\alpha$ -position. In mild acid treatment, 2-acetyl-2-nitrosopropane loses the acetyl group<sup>70</sup> (equation 151). A similar reaction in base has been reported for the benzoyl analog<sup>244</sup> (equation 152). The ring-expansion of



2-alkyl-2-nitroso-1-indanones to isocarbostyryl derivatives may follow a related path<sup>244</sup> (equation 153).

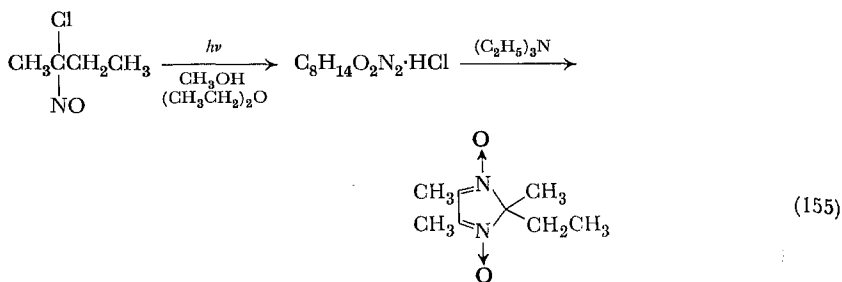


An incompletely understood acid hydrolysis converts 2-chloro-2-nitrosobutane into a mixture of the oxime of butanone-2 and the monoxime of butanedione-2,3<sup>245</sup> (equation 154). It has been



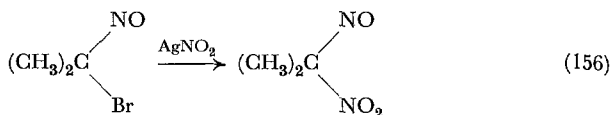
suggested that these two oximes are first formed in the photolytic transformation of the geminal nitrosochloride into an imidazole-di-N-oxide<sup>245</sup> (equation 155).

Aliphatic carboxylic acids in oleum are nitrosated at the  $\alpha$ -position and decarboxylated on treatment with nitrosyl sulfuric acid, cf. II.J. When  $\alpha$ -hydrogen is present decarboxylation from an



oxime would account for the product, an aldoxime<sup>67</sup>; but in the nitrosative decarboxylation of an aromatic acid decarboxylation from a tertiary nitroso compound is proposed, cf. II.J.

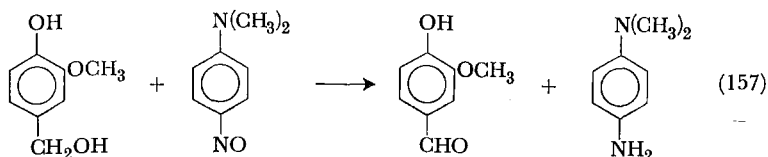
There is at least one example of  $\alpha$ -halogen displacement<sup>108</sup> (equation 156). The electron-withdrawing power of the nitroso



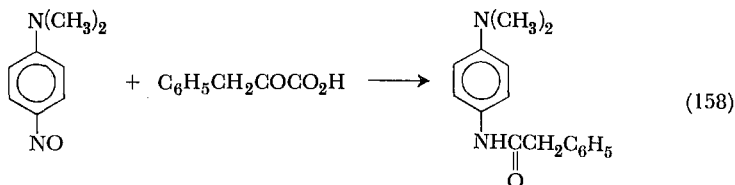
group has been demonstrated with *p*-bromonitrosobenzene which reacts more rapidly with silver nitrate solution than *p*-bromonitrobenzene does<sup>246</sup>.

## E. Reduction

Over platinum<sup>247, 248</sup>, nickel<sup>249</sup>, palladium<sup>250, 251</sup> and other catalysts aliphatic and aromatic nitroso compounds are generally reduced to primary amines. A reported incomplete reduction with the formation of cyclohexylhydroxylamine from nitrosocyclohexane dimer over a catalyst is exceptional<sup>217</sup>. Metal and acid combinations and certain lower valent metal salts also give reduction to the corresponding amine. Common examples include tin in hydrochloric acid or stannous chloride<sup>252-255</sup> or zinc dust in acid<sup>256</sup>. Concentrated hydrochloric acid both reduces and halogenates nitrosobenzene to form chloroazoxybenzene, trichloroaniline, chlorophenylhydroxylamine and other products<sup>257</sup>. Sodium bisulfite reduced *p*-nitrosotoluene to *p*-toluidine and also sulfonated the ring<sup>163</sup>. Hydroiodic acid transformed *p*-nitrosodimethylaniline into *p*-aminomethylaniline by simultaneous reduction and demethylation<sup>258, 259</sup>. Oxidation of vanillyl alcohol to vanillin may be brought about with *p*-nitrosodimethylaniline<sup>260</sup> (equation 157). Phenylpyruvic acid<sup>261</sup> and *N*-

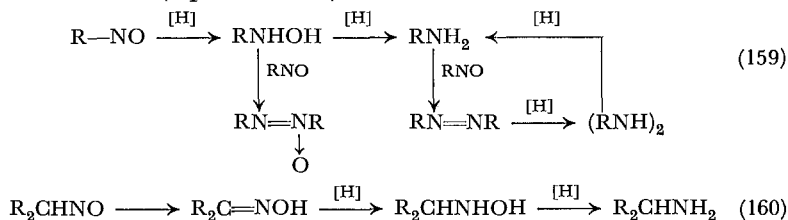


benzyl-1,4-dihydronicotinamide<sup>262</sup> also reduce *p*-nitrosodimethyl-aniline to a primary amine (equation 158) but pyruvic acid reduces the nitroso compound to the corresponding azoxy derivative<sup>261</sup>.



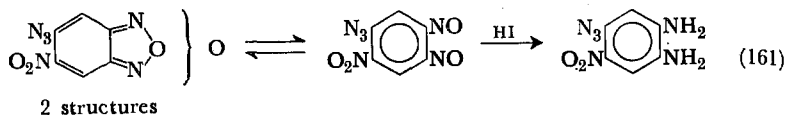
With varying degrees of control over product formation aromatic nitroso compounds are reduced to mixtures of amines, azo, azoxy and hydrazocompounds by alcoholic alkali or alkoxide<sup>263</sup>, formaldehyde<sup>264</sup>, hydrazine<sup>265</sup>, formamide<sup>266</sup>, hydrogen sulfide<sup>267</sup>, trivalent molybdenum<sup>268</sup>, zinc diethyl<sup>269</sup>, arsenites<sup>270</sup>, sodium borohydride<sup>271</sup>, phenyl mercaptan<sup>272</sup>, lithium aluminum hydride<sup>273</sup> and other reagents. A deficient amount of lithium aluminum hydride transforms nitrosobenzene into diphenylnitric oxide, detected and identified by its e.s.r. spectrum<sup>273</sup>. The photoreduction of nitrosobenzene in methanol, ethanol or benzene gives primarily azoxybenzene but also its *p*-nitro-, *o*-hydroxy and *p*-hydroxy derivatives, diphenylamine and nitrodiphenylamines<sup>274,275</sup>. Each of these latter two methods of reducing nitrosobenzene require cleavage and reformation of a C—N bond. An enzymatic reduction of *p*-nitrosobenzoic acid to *p*-aminobenzoic acid has been observed<sup>276</sup>.

A summary of the reduction paths is helpful<sup>277</sup> (equation 159). With each example isomerization of the nitrosoalkane to an oxime may be more rapid than reduction and, if so, will alter the course of the reduction (equation 160).



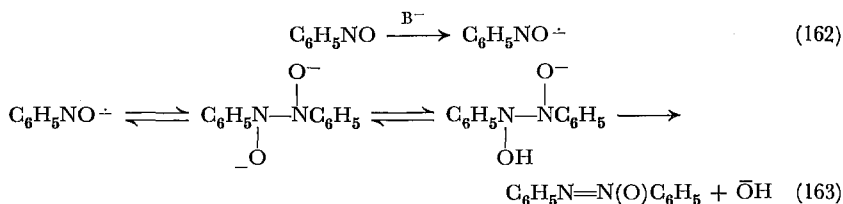
Reductive alkylation transforms nitrosobenzene into *N,N*-dipropylaniline in a reaction with propionaldehyde and hydrogen over nickel<sup>278</sup>. Ketones require more drastic treatment.

Hydroxylamine reduces both *o*-dinitrosobenzene (benzfuroxan) and its *para*-isomer to the corresponding dioximes<sup>116,279</sup>. The sensitivity of nitroso groups toward reduction is revealed in the transformation of 1,2-dinitroso 4-azido-5-nitrobenzene by hydrogen iodide into 1,2-diamino-4-azido-5-nitrobenzene<sup>280</sup> (equation 161). Copper in the presence of an acid reduces *o*-dinitrosobenzene, cf. III.O., to *o*-nitroaniline and isomerizes *o*-benzoquinone dioxime

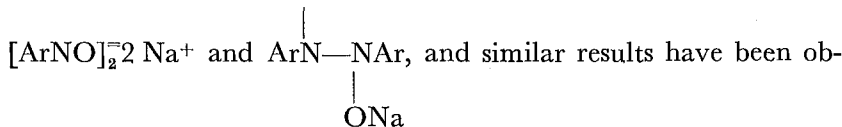


into the same product<sup>281</sup>. A similar over-all reduction of the sodium salt of the bisulfite adduct of 1,2-dinitrosonaphthalene-6-sulfonic acid in dilute sodium carbonate solution to a disodium salt of 1-amino-2-nitronaphthalene-4,6-disulfonic acid has been observed<sup>282</sup>.

Aromatic thiolate anions and the *t*-butoxide anion transform nitrosobenzene into its radical anion as determined by esr measurements<sup>283</sup> (equation 162) and is the first step in the reduction of nitrosobenzene to azoxybenzene<sup>284</sup> (equation 163). Aromatic nitroso



compounds react with sodium in ether to produce<sup>285</sup>  $[\text{ArNO}]^{\cdot-} \text{Na}^+$ ,



tained with lower valent aluminum and unipositive magnesium<sup>286</sup>.

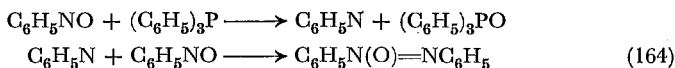
The radical anion of nitrosobenzene is also formed in the first polarographic reduction step conducted in 0.2 *N* sodium nitrate in dimethylformamide. When oxygen is present nitrobenzene is formed whereas in the absence of oxygen, azoxybenzene is the final



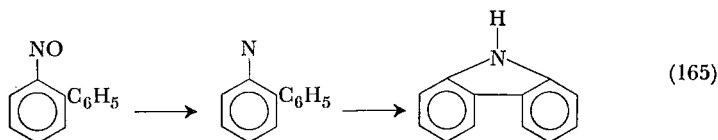
product<sup>287</sup>. The reversible reduction of nitrosobenzene to phenylhydroxylamine is a two-electron process<sup>288,289</sup> in which the redox potential varies with pH. The variation of the half-peak potential (vs. S.C.E.) over a pH range from 1.6 to 12.5 at 25° is given by  $E_{\frac{1}{2}} = 0.33 - 0.060 \text{ pH}^{290}$ .

### F. Deoxygenation

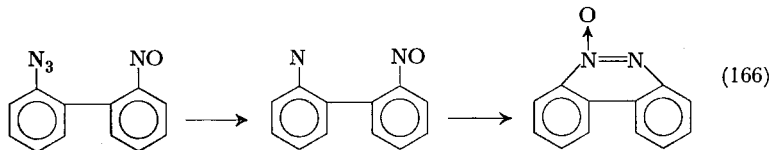
Deoxygenation of a nitroso compound may provide a nitrene intermediate. An explanation for the formation of azoxybenzene on treating nitrosobenzene with triphenylphosphine requires deoxygenation to phenyl nitrene and subsequent combination with nitrosobenzene<sup>291</sup> (equation 164). In other examples the nitrene may prefer an intramolecular reaction. Cyclization of *o*-biphenyl



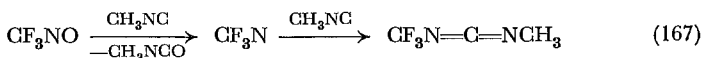
nitrene, an assumed intermediate, accounts for the formation of carbazole in a reaction between *o*-nitrosobiphenyl and triphenylphosphine<sup>292</sup> (equation 165). The intermediacy of a nitrene has been



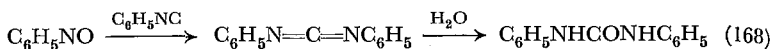
assumed in both the photolytic and the pyrolytic conversion of *o*-nitroso-*o'*-azidobiphenyl into benzocinnoline-*N*-oxide<sup>293</sup> (equation 166).



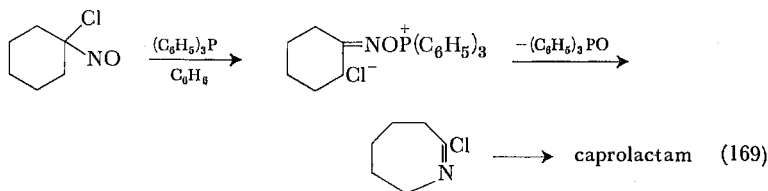
An isonitrile may deoxygenate a nitroso compound and apparently can combine with an intermediate nitrene with the formation of a carbodiimide. *N*-Trifluoromethyl-*N'*-methylcarbodiimide is obtained from trifluoronitrosomethane and methyl isonitrile<sup>194</sup> (equation 167). The earlier work of Passerini<sup>294,295</sup> in which *N,N'*-



diphenylurea was obtained from nitrosobenzene and phenyl isonitrile is easily accounted for by a similar reaction leading to the formation of diphenylcarbodiimide followed by hydration (equation 168).



Deoxygenation and ring-enlargement occur when *gem*-chloronitrosocyclohexane is treated with triphenylphosphine in benzene. An explanation which has been offered may not require the intermediacy of a nitrene<sup>296</sup> (equation 169).



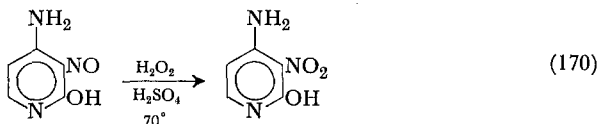
### G. Oxidation

Nitric acid<sup>297</sup>, hydrogen peroxide<sup>298</sup>, permanganate<sup>299</sup>, chromic oxide<sup>300</sup>, persulfuric acid<sup>300</sup>, ammonium persulfate<sup>301</sup>, hypochlorite<sup>300</sup>, peroxyacetic acid<sup>302</sup>, peroxytrifluoroacetic acid<sup>303</sup>, ozone<sup>304</sup> and other reagents oxidize nitroso compounds to nitro compounds. The reaction, generally limited to tertiary aliphatic and aromatic nitroso derivatives, often leads to several products. In strong nitric acid, nitrosobenzene is transformed into nitrobenzene, *p*-dinitrosobenzene, *p*-nitrophenol, 2,4-dinitrophenol, picric acid and oxalic acid<sup>305</sup>.

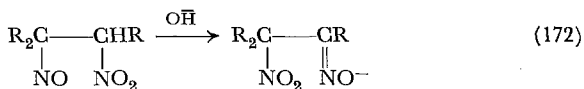
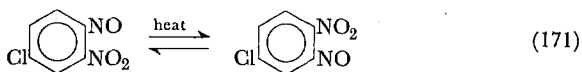
With first-order dependence on each reactant, nitrosobenzenes are oxidized by peroxyacetic acid in aqueous ethanol to corresponding nitrobenzenes<sup>302</sup>. The reaction is accelerated by electron-releasing *p*-substituents and by changing the solvent from ethanol to water, and it is decelerated by electron-withdrawing *p*-substituents. Apparently a greater acidity in the peroxy acid enhances the reaction; peroxychloroacetic and Caro's acid each oxidize nitrosobenzene more rapidly than does peroxyacetic acid. A mechanism consistent with these facts calls for a reaction initiated by a nucleophilic attack of the nitroso nitrogen on the outer oxygen of the peroxy acid with a transition state composed of the peroxy acid, the nitroso compound and a solvent molecule. This mechanism is also supported by the direction and magnitude of the substituent effect

( $\rho -1.58$ ), the activation parameters for nitrosobenzene ( $E_a$  16.1 kcal mole<sup>-1</sup>,  $\Delta S^\ddagger -22$  cal mole<sup>-1</sup> deg<sup>-1</sup>), and the absence of acid catalysis.

The resistance of *m*-trifluoromethylnitrosobenzene toward oxidation by permanganate, dichromate or hydrogen peroxide in acetic acid<sup>165</sup> is not typical and gives a striking contrast with the facile oxidation of the nitroso group in 2-hydroxy-3-nitroso-4-aminopyridine by hydrogen peroxide in sulfuric acid<sup>59,306</sup> (equation 170).

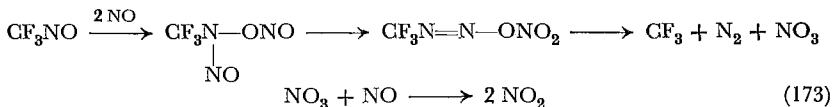


An intramolecular transfer of oxygen between nitroso and nitro groups *ortho* to each other in aromatic compounds or on adjacent paraffinic carbon atoms is thermally produced in one instance and base-catalyzed in the other (equations 171, 172). The intermediacy of a furoxan oxide and a dihydrofuroxan oxide respectively may be required<sup>307,308</sup>.

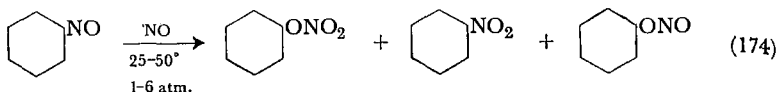


## H. Free Radicals

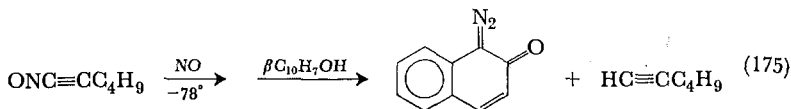
Free radicals tend to attack the nitroso group in pairs in a reaction leading to the formation of an *O,N*-disubstituted hydroxylamine. The adduct from trifluoronitrosomethane and two molecules of nitric oxide has been isolated<sup>309,310</sup>; however, the reaction usually proceeds at higher temperatures with rearrangement to a diazonium nitrate and subsequent decomposition<sup>311</sup> (equation 173). Certain aliphatic nitroso compounds combine with nitric oxide to form



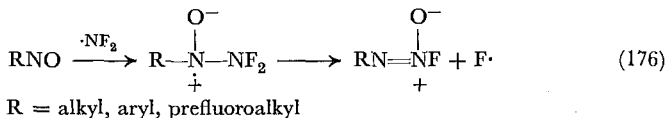
corresponding nitro compounds and nitrate esters along with trace amounts of nitrite esters<sup>255,312</sup> (equation 174). Presumably, a dinitrosohydroxylamine and a diazonitrate are intermediates.



$\beta$ -Naphthol is transformed into a diazooxide on addition to the reaction mixture in which 1-nitrosohexyne-1 is treated with nitric oxide in methylene chloride at low temperature<sup>313</sup> (equation 175). On similar treatment, dimethylaniline is transformed into its *p*-nitro and *p*-diazonium salt derivatives.



Many, but not all, radicals readily react with the nitroso group. Nitrosobenzene has an exceptionally high 'methyl affinity' (ca  $10^5$ )<sup>314</sup> but has less tendency to react with triphenylmethyl<sup>315</sup>. It has been reported that nitrosobenzene reacts with triphenylmethyl in benzene to produce triphenylcarbinol and *p,p'*-ditriphenylmethylazoxybenzene<sup>316</sup>. The formation of trimethylhydroxylamine from nitrosomethane and methyl radicals at room temperature has been demonstrated<sup>317</sup>. In contrast, apparently neither an *O,N*-dinitrosohydroxylamine nor a triperfluoroalkylhydroxylamine has been detected during the dimerization of a perfluoronitrosoalkane which presumably proceeds with the initial formation of a nitric oxide and a perfluoroalkyl with subsequent addition of each to an unchanged perfluoronitrosoalkane, cf. III.A. A radical mechanism was proposed to explain the formation of *N*-trifluoromethyl-*N'*-fluorodiimide oxide from either the photochemical or the thermal reaction of trifluoronitrosomethane and tetrafluorohydrazine<sup>318</sup> (equation 176).



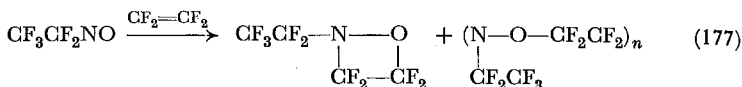
R = alkyl, aryl, prefluoroalkyl

The high efficiency of *p*-nitrosodimethylaniline as a scavenger for the hydroxyl radical<sup>319</sup> further demonstrates the affinity the nitroso group has for radicals.

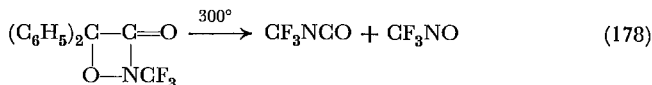
### I. Monoolefins

Both oxazetidines and copolymers are formed in reactions between perfluoroolefins and perfluoro nitroso derivatives<sup>320</sup> (equation 177).

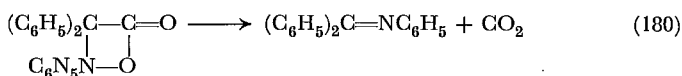
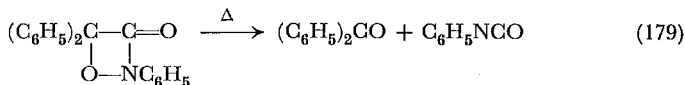
At lower temperatures polymer formation may predominate. Pyrolysis of the oxazetidinone from diphenylketene and trifluoro-



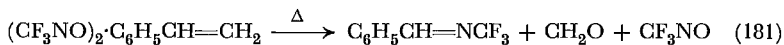
nitrosomethane gives both trifluoromethyl isocyanate and trifluoronitrosomethane<sup>194</sup> (equation 178). Apparently two oxazetidinones resulted from the combination of diphenyl ketene and nitroso-



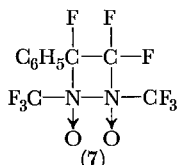
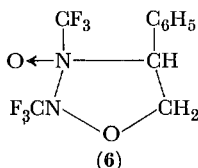
benzene. Pyrolysis of one gave benzophenone and phenyl isocyanate; the other was less stable and readily dissociated into carbon dioxide and benzophenone anil<sup>321</sup> (equations 179, 180);



Trifluoronitrosomethane gives a 1:1 adduct with ethyl azodicarboxylate and both a 1:1 and a 2:1 adduct with styrene<sup>194</sup>. The latter equimolar adduct undergoes pyrolysis with the formation of trifluoronitrosomethane, formaldehyde and the Schiff base of trifluoromethylamine and benzaldehyde (equation 181). A 2:1 adduct

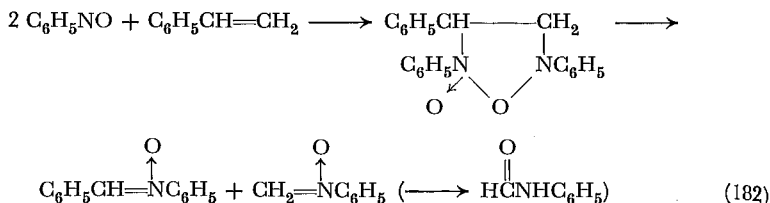


obtained from trifluoronitrosomethane and trifluorostyrene<sup>323</sup> also releases trifluoronitrosomethane on heating. From nmr data the first of the 2:1 adducts has been assigned the structure of a tetrahydro-(1,2,3)-oxadiazole (6) and the latter the structure of a 1,2-diazacyclobutane<sup>323</sup> (7). These adducts are structurally different



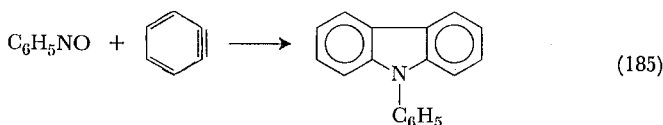
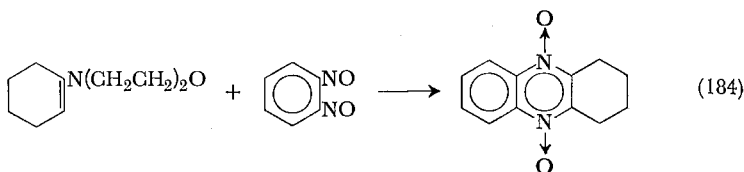
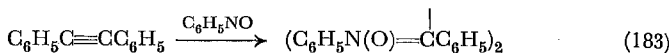
from the adduct which has been obtained from nitrosobenzene and styrene and has been shown to be an unstable tetrahydrofuroxan

which dissociates into nitrones<sup>324</sup> (equation 182).



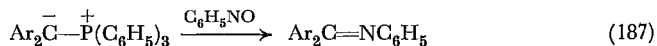
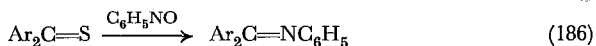
### J. Acetylenes and Arynes

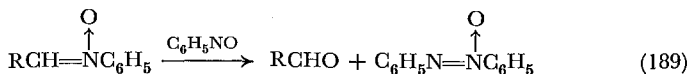
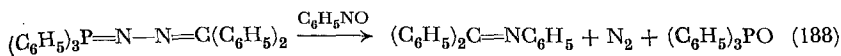
Certain acetylenes combine with two moles of a nitroso compound to give vicinal *bis*-nitrones<sup>325</sup> (equation 183). A *bis*-nitrone, 1,2,3,4-tetrahydrophenazine-*N,N'*-dioxide is also obtained from 1-morpholinocyclohexene and *o*-dinitrosobenzene (benzfuroxan)<sup>326</sup> (equation 184). Other eneamines gave similar reactions. Nitrosobenzene adds to benzyne in a more complicated reaction which leads to the formation of *N*-phenylcarbazole<sup>327</sup> (equation 185).



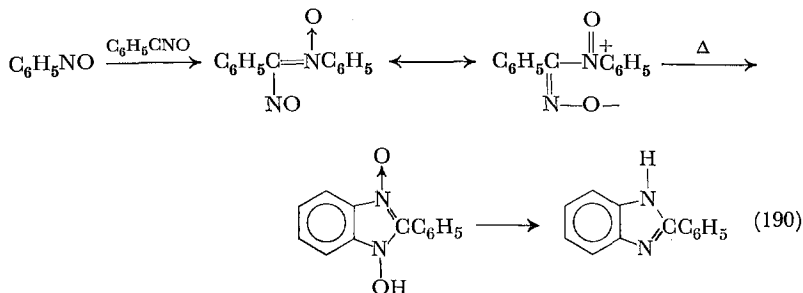
### K. Thioketones, Phosphorous Ylids, Azomethine Derivatives

Nitrosobenzene combines with a variety of doubly unsaturated bonds connecting carbon to a heteroatom (equations 186, 187, 188, 189), but it is not known whether these reactions proceed with the initial formation of four-membered rings<sup>328,329</sup>. The cleavage of nitrones by nitrosobenzene (equation 189) is apparently slow since nitrones are often prepared by reactions of nitroso compounds.



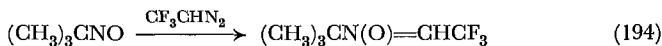
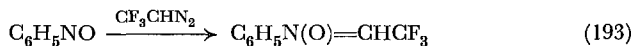
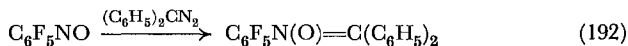
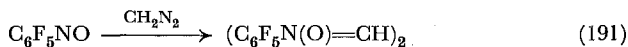


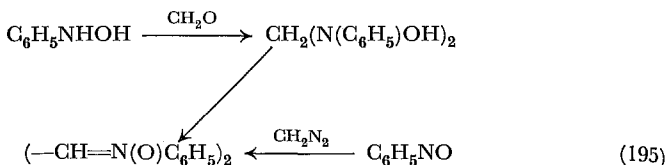
As a nucleophile, nitrosobenzene combines with benzonitrile oxide to produce a nitrosonitrone<sup>330</sup> (equation 190). On mild heating the latter cyclizes.



### L. Diazoalkanes

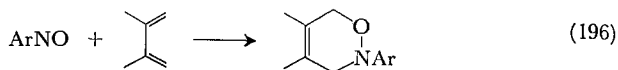
Many combinations of nitroso compounds and diazoalkanes lead to nitrones<sup>331</sup> (equations 191, 192, 193, 194). In the reaction with diazomethane oxidation may occur and the product is a *bis*-nitrone (equation 191). The same nitrone is obtained from the reaction between formaldehyde and phenylhydroxylamine and from the reaction between diazomethane and nitrosobenzene<sup>332</sup> (equation 195). It has been suggested that the reaction proceeds by electrophilic attack of nitroso nitrogen upon diazoalkane carbon<sup>333</sup>. This is in agreement with the formation of an adduct between trifluoronitrosomethane and diazomethane which subsequently loses nitrogen<sup>194</sup>. On treatment with diazomethane, the reduction of nitrosomesitylene to the corresponding hydroxylamine<sup>334</sup> may have proceeded with the initial formation of a nitrone followed by the Kröhnke reaction, cf. III.R, in which the nitrone is cleaved to an aldehyde and a derivative of hydroxylamine.



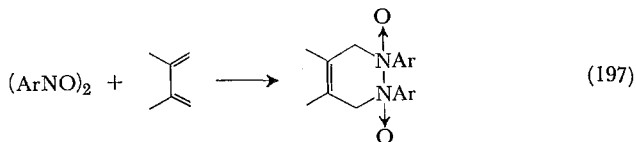


### M. Conjugated Dienes

Dihydro-1,2-oxazines are readily obtained from aromatic nitroso compounds and conjugated dienes. The addition of an aromatic nitroso compound to 2,3-dimethyl-1,3-butadiene follows first order kinetics in each reactant with low activation energies (14.23 kcal/mole for nitrosobenzene)<sup>335</sup> (equation 196). Nitroso dimers may com-

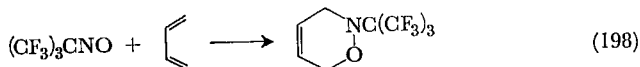


bine with dienes with the formation of tetrahydropyridazine-*N,N'*-dioxides<sup>336</sup> (equation 197).



An unsymmetrically substituted diene may combine with a nitroso monomer to give a mixture of the two expected structural isomers<sup>337</sup>. Apparently the monosubstituted 1-arylbutadienes give exclusively the dihydrooxazines in which oxygen is attached to the benzylic carbon; the disubstituted 1-phenyl-4-carbomethoxybutadiene gives the isomer in which nitrogen is attached to the benzylic carbon<sup>338</sup>. Nitrosobenzene failed to react with anthracene<sup>339</sup>.

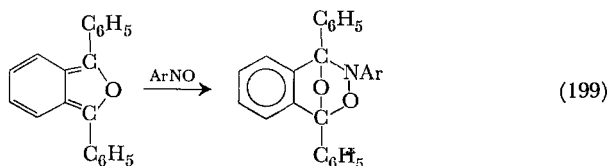
Aliphatic nitroso compounds are more resistant to dienes; 2-methyl-2-nitrosopropane failed to react with 2,3-dimethylbutadiene<sup>133,139</sup> however, its perfluoro analog combined with butadiene over a three day period in a sealed tube<sup>340</sup> (equation 198).



Both  $\alpha$ -halo- and  $\alpha$ -cyanonitrosoalkanes also combine with dienes to give the expected dihydrooxazine<sup>133</sup>. The resistance of both 1-chloro-1-nitrosocyclohexane and nitrosobenzene to react with

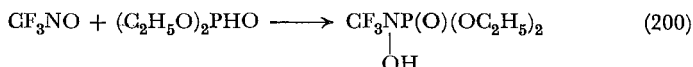


2,3-diphenyl-, 1,1-diphenyl-, and 1,2,3,4-tetraphenylbutadiene -1,3 may be attributed to a combination of steric and electronic effects<sup>341</sup> but a steric hindrance does not prevent the addition of aromatic nitroso compounds to 1,3-diphenylisobenzofuran<sup>342</sup> (equation 199) or to tetraphenylcyclopentadienone<sup>343</sup>.

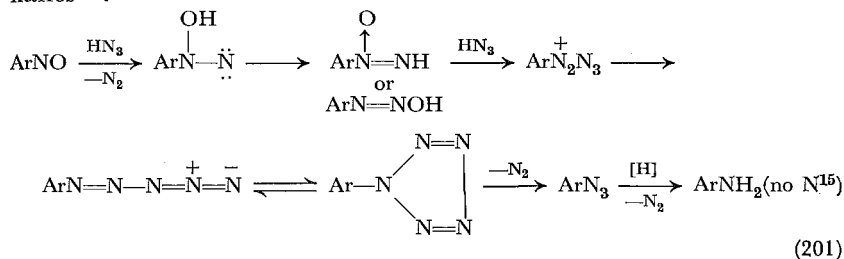


## N. Compounds with Active Hydrogen

A compound which contains an active hydrogen may add in the expected manner to a nitroso group; diethyl acid phosphite adding to trifluoronitrosomethane gives an example<sup>344</sup> (equation 200). The nitroso group may also combine with hydrogen azide. From aro-

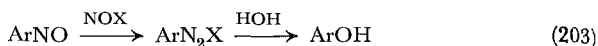
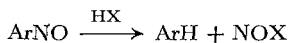


matic nitroso compounds the corresponding aryl azides are often obtained in good yield. As expected, electron withdrawing ring substituents facilitate the reaction. In support of both a linear and a cyclic pentazene intermediate<sup>345</sup>, it has been shown by isotopic labeling that the two outer nitrogens in the product azide are derived from the outer nitrogens in hydrogen azide (equation 201). The reaction has been extended to the preparation of  $\alpha$ -nitroazidoalkanes<sup>346</sup>.

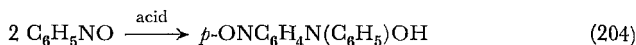


Nitrosobenzene is feebly basic ( $\text{p}K_a \simeq 0$  at  $25^\circ$  in absolute methanol)<sup>347</sup>; nevertheless, aliphatic and aromatic nitroso compounds are sufficiently nucleophilic to form adducts with *p*-toluenesulfonic acid<sup>328</sup>, hydrogen chloride<sup>28,348,349,350</sup> and hydrogen bromide<sup>350</sup>.

Presumably the adducts are hydroxylamines (equation 202). In one instance a nitrosotoluene was transformed into a cresol by mineral acid conceivably by cleavage to a nitrosyl halide followed by diazotization of unchanged nitrosotoluene and hydrolysis<sup>348,349</sup> (equation 203). This agrees with the demonstration of the reversibility of nitrosation at carbon in which *p*-nitrosodimethylaniline was produced in an alcoholic hydrogen chloride solution of *p*-nitrosodiphenylamine and dimethylaniline<sup>351</sup>. Concentrated sulfuric<sup>352</sup>, hydrofluoric<sup>353</sup> or peroxytrifluoroacetic acid<sup>303</sup> may catalyze

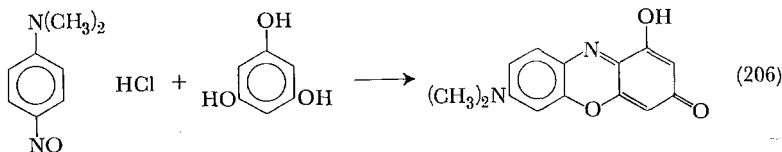
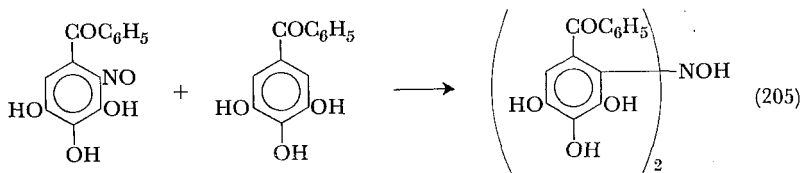


an addition of nitrosobenzene to itself (equation 204). Similar



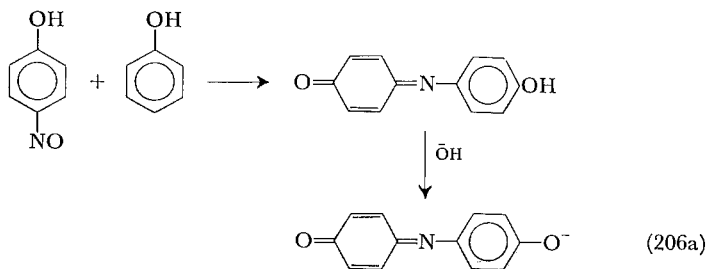
condensations occur with *o*- and *m*-substituted derivatives of nitrosobenzene<sup>352</sup>, but more complicated reactions occur when a substituent is *para* to the nitroso group. From *p*-nitrosotoluene in concentrated sulfuric acid in acetic acid, dimethylphenazine oxide, dimethylphenazine, *p*-azoxytoluene, *p*-azotoluene and unidentified compounds are obtained<sup>354</sup>.

Phenols combine with nitroso compounds with the generation of a new carbon-nitrogen rather than a new oxygen-nitrogen bond<sup>355</sup> (equations 205, 206). Ring-closure to phenoxazine derivatives may follow.



There are at least two condensations with phenols which have been developed in qualitative detection of the nitroso group. On

treatment of a nitroso compound with a one percent solution of resorcinol in concentrated hydrochloric acid, a blue-violet color develops which after dilution with water, and extraction with ether, gives a red color<sup>355</sup>. In the other test, C-nitroso compounds, from which nitrous acid is eliminated upon treatment with concentrated sulfuric acid, give Liebermann's test with alkaline phenol. The nitrous acid reacts with the phenol to give *p*-nitrosophenol, which condenses with more phenol to give indophenol; when the product is poured into alkali, the blue color of the anion appears<sup>355b</sup> (equation 206a).



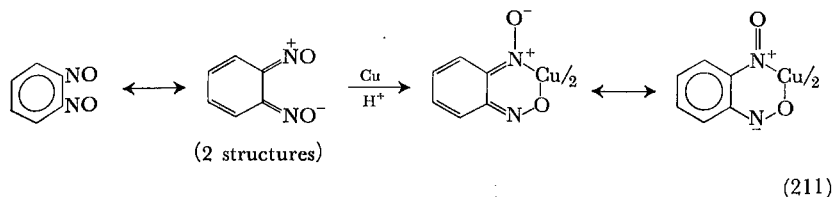
### O. Complexes with Metal Salts and Lewis Acids and Metal Chelates

Certain nitroso bases give colored precipitates of the corresponding ferro- and ferricyanide complexes. For example, *p*-nitroso-*N,N*-dimethylaniline ferrocyanide precipitates in red-brown needles which appear blue by reflected light<sup>356</sup>. Sunlight irradiation of a potassium ferrocyanide solution with aromatic nitroso compounds first gives a red color followed by the formation of a complex salt with RNO of the type<sup>357</sup>  $\text{K}_3[\text{Fe}(\text{CN})_5 \cdot \text{RNO}]$ . A similar exchange reaction between  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$  and RNO is brought about by sunlight and is accompanied by a color change from bright yellow to violet or green and has been used for the detection of aromatic nitroso compounds<sup>358</sup>.

Complex salts from nitroso compounds and certain metallic halides have been noted in several instances. The green solution of nitrosobenzene, when mixed with an alcoholic solution of cadmium iodide, slowly deposits very small colorless crystals of the salt<sup>359</sup>,  $(\text{C}_6\text{H}_5\text{NO})_5 \cdot \text{CdI}_2$ . With bismuth trichloride and *p*-nitroso-*N,N*-dimethylaniline, a similar complex,  $2[p\text{-NOC}_6\text{H}_4\text{N}(\text{CH}_3)_2] \cdot 3 \text{BiCl}_3$ , is formed<sup>360</sup>. Yellow amorphous complexes have been reported<sup>361</sup> for  $2 \text{C}_6\text{H}_5\text{NO} \cdot \text{SnCl}_4$  and  $2 \text{C}_6\text{H}_5\text{NO} \cdot \text{TiCl}_4$ . By the direct addition of

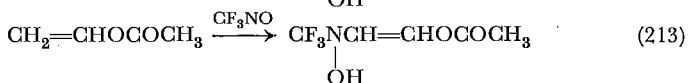
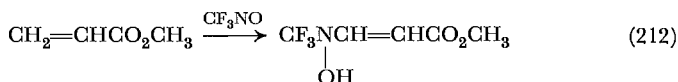


In the presence of acid, copper combines with the ring-opened isomer, *o*-dinitrosobenzene, of benzfuroxan<sup>281</sup> (equation 211).

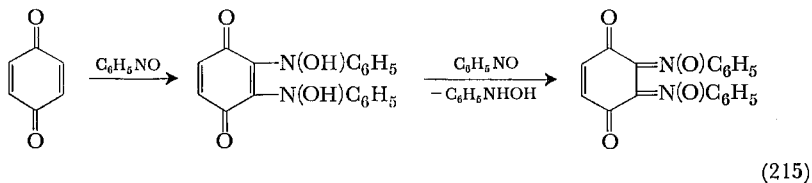
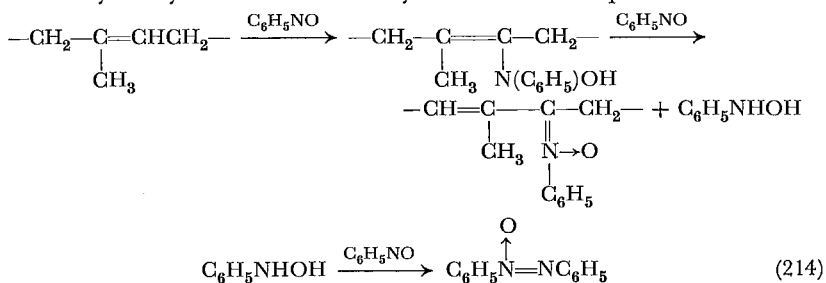


***P. Methylene and Methynyl Groups in Olefins, Schiff Bases, Carbonyl Compounds***

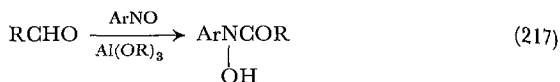
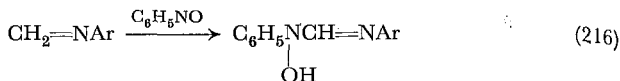
Certain olefins which do not combine with the nitroso group to give oxazetidines, cf. III.I, and have hydrogen attached to olefinic carbon may add to the nitroso double bond with the formation of an *N,N*-disubstituted hydroxylamine<sup>323</sup> (equations 212, 213). The reaction in which three molecules of nitrosobenzene combine with a



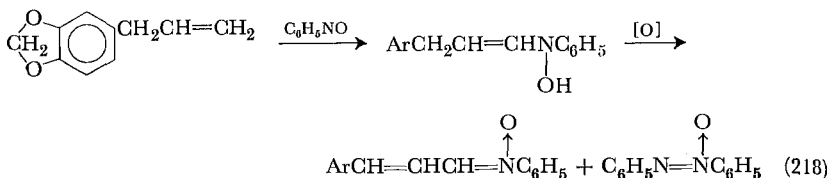
C<sub>6</sub>H<sub>8</sub> unit in rubber may require an initial addition of this kind with subsequent oxidation to a nitron and azoxybenzene<sup>369</sup> (equation 214). The *bis*-nitron obtained from nitrosobenzene and *p*-benzoquinone<sup>370</sup> (equation 215) may also require initially the formation of a *bis*-hydroxylamine since azoxybenzene is also produced.



A similar attack by nitroso nitrogen on a terminal methylene group in an azomethine linkage has been described<sup>371</sup> (equation 216). Probably the base catalyzed addition of an aldehyde to the nitroso group is a related reaction<sup>372</sup> (equation 217). Safrole reacts with nitrosobenzene to give a nitrone and azoxybenzene; presumably the

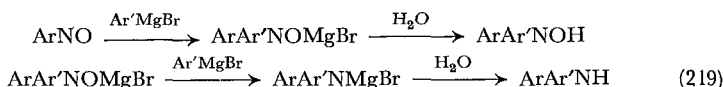


expected hydroxylamine is an intermediate<sup>373</sup> (equation 218).

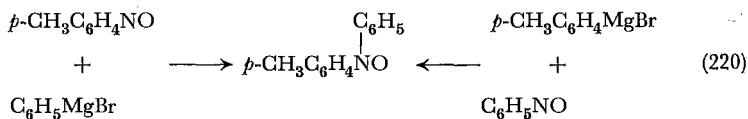


### Q. Grignard Reagents

The early work of Wieland demonstrated the initial formation of an *N,N*-disubstituted hydroxylamine salt which subsequently may be reduced by an excess of the Grignard reagent to a secondary amine<sup>374,375</sup> (equation 219). Hydroxylamines were not isolated from



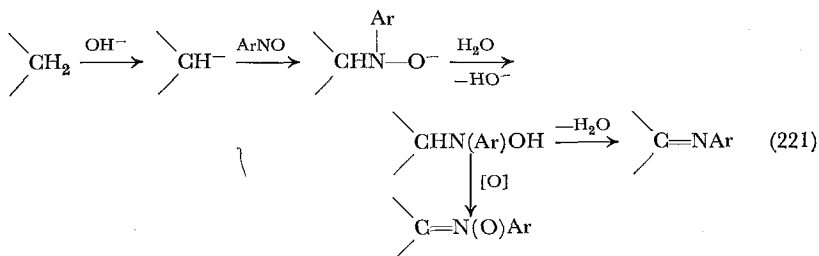
nitrosobenzenes in which powerful electron-donating groups such as methoxy and dimethylamino occupied the *para*-position and further reaction leading to the expected secondary amine was detected<sup>375</sup> as well as reduction to corresponding azobenzenes<sup>376</sup>. The formation of intermediate nitroso radical anions<sup>377</sup> appears probable but would not be required for the formation of *p*-tolylphenylnitric oxide from either *p*-nitrosotoluene with phenylmagnesium bromide or nitrosobenzene with *p*-tolylmagnesium bromide<sup>378</sup> (equation 220). Both dialkylzinc and alkyl Grignard reagents transform 2-halo-2-



nitrosopropane into products of dehydrohalogenation, reduction and condensation<sup>379</sup>.

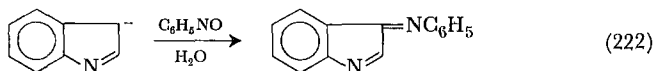
### R. Ehrlich-Sachs Reaction

A base catalyzed condensation between an active methylene group and the nitroso group attached to an aromatic ring is known as the Ehrlich-Sachs reaction<sup>380</sup>. It is presumably initiated by a nucleophilic attack by the corresponding carbanion on nitroso nitrogen. Dehydration of an assumed intermediate hydroxylamine gives the expected product, an anil, in competition with oxidation to a nitron (equation 221). Unreacted nitroso compound may serve as the oxidizing agent and is thereby reduced to an azoxy compound or an amine. The catalyst is usually provided by an aqueous alcoholic soda solution but sodium alkoxides<sup>381,382</sup>, alkali<sup>383</sup>, piperidine<sup>384</sup>, potassium cyanide, trisodium phosphate and other bases have been effective. In general the reaction leads to a mixture and there is limited success in predicting a predominance of dehydration or of oxidation product. Typical examples of compounds containing an active methylene group which participates in the Ehrlich-Sachs

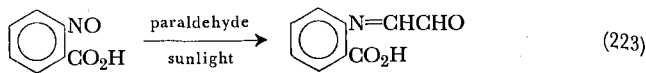


reaction include benzyl cyanide, 2,4-dinitrotoluene<sup>384</sup>, certain cyclopentadienes<sup>385</sup>, benzyldiphenylphosphine oxide<sup>382</sup>, indole<sup>386</sup> and certain other heterocycles<sup>387</sup>.

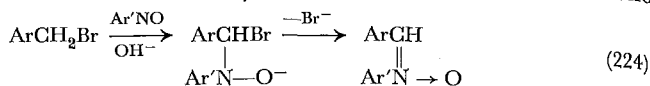
For an example of a postulated intramolecular condensation of an *o*-nitroso-*N,N*-dimethylaniline leading to the formation of the corresponding *N*-methylimidazole see II.V. In the condensation with indole the required anion is one expression of the resonance anion of indole (equation 222). An unidentified product, C<sub>9</sub>H<sub>7</sub>O<sub>3</sub>N,



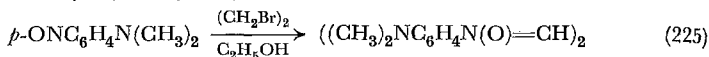
formed in the absence of base from paraldehyde and *o*-nitrosobenzoic acid exposed to sunlight may be the expected anil<sup>388</sup> (equation 223).



Benzyl and certain other halides also condense with aromatic nitroso compounds to give nitrones<sup>383</sup> (equation 224) by a reaction sequence in which initial attack by either a carbanion or a carbene

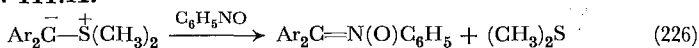


seems plausible. Additional base is not required for the condensation between *p*-nitrosodimethylaniline and ethylene dibromide. The product, identical with the *bis*-nitrone obtained from *p*-nitrosodimethylaniline and diazomethane<sup>389</sup> (equation 225), cf. III.L., is transformed into *bis*-dimethylaminoazoxybenzene on being heated with *p*-nitrosodimethylaniline in ethanol. A preparation of aldehydes from nitrones by hydrolysis (Kröhnke reaction) calls for a variation



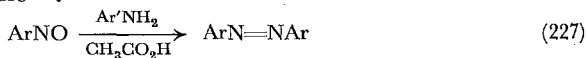
in the nitrone synthesis in which the halide is first transformed into its pyridinium salt<sup>390</sup>.

Sulfonium ( $\text{R}_2\text{S}^+-\text{CR}_2^-$ ) and phosphonium ylides readily combine with nitrosobenzene to give a nitrone and a sulfide in the former examples<sup>391</sup> (equation 226) and an anil and a phosphine oxide in the latter<sup>328</sup>, cf. III.K.



### S. Amines, Hydroxylamines, Hydrazines

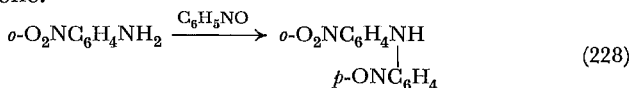
Amines, hydrazines and hydroxylamines are additional reagents which may attack the nitroso nitrogen. Azo compounds are formed in the condensation of primary aromatic amines with aromatic nitroso compounds generally carried out under mild conditions in acetic acid<sup>392</sup> (equation 227). Unsymmetrically substituted azo compounds are readily obtained; *p*-toluidine and nitrosobenzene or aniline and *p*-nitrosotoluene give nearly the theoretical amount of benzene-azo-*p*-toluene<sup>393</sup>.



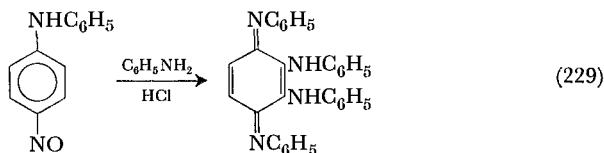


From a kinetic study a rate determining step in which protonated or acid-activated nitrosobenzene attacks nitrogen of free aniline in acetic acid has been postulated<sup>394</sup> with the recognition that a protonated *N*-anilinoxyhydroxylamine may be an intermediate. Oxidation of the intermediate accounts for the formation of corresponding azoxy compounds as by-products<sup>395</sup>.

In reaction with *m*- and *p*-nitroaniline, nitrosobenzene gives the expected azo compound; but *o*-nitroaniline combines with nitrosobenzene to give *o*-nitro-*p'*-nitrosodiphenylamine<sup>392</sup> (equation 228). It is reported that *o*-nitroaniline does not react with either *o*- or *m*-nitronitrosobenzene.



The condensation may lead to interesting variations as the following three reactions will illustrate. (1) An unidentified product,  $\text{C}_{26}\text{H}_{18}\text{ON}_2$ , was obtained from nitrosobenzene and  $\alpha$ -naphthylamine<sup>396</sup>. (2) Aniline condenses with each nitroso group in derivatives of *p*-dinitrosobenzene to give both the expected *bis*-azo- as well as the azoazoxy-products<sup>397</sup>. (3) Azophenine is obtained on treating *p*-nitrosodiphenylamine with aniline in the presence of its hydrochloride<sup>398</sup> (equation 229).

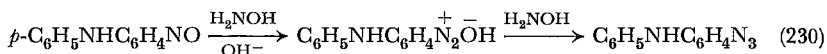


There is a lack of information on possible reactions between primary aliphatic amines and nitroso compounds. Dilute aqueous ethylamine reacts with 1-nitroso-2-naphthol to give 1-nitroso-2-*N*-ethylaminonaphthalene<sup>399,400</sup> and no product was reported which would indicate a reaction at the nitroso group. In general aromatic nitroso amines are produced by digesting nitrosophenols with hot solid ammonium chloride and ammonium acetate<sup>401</sup>. Secondary amines may react in a complicated way with nitrosobenzene to give azobenzene, nitrobenzene, aniline and azoxybenzene. A small portion of the amine is changed into an *N,N*-dialkylhydroxylamine which also appears to be formed when nitrosobenzene is heated for a long time with a tertiary amine<sup>402</sup>. It would appear that secondary amines are not highly reactive toward the nitroso group since

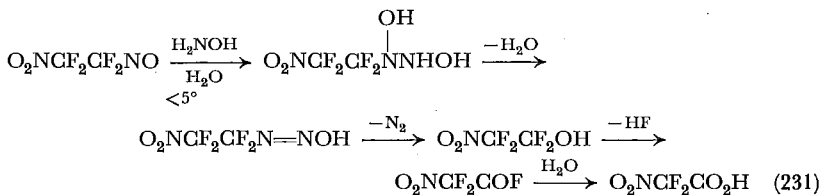
piperidine is sometimes employed as a catalyst for other reactions. In concentrated sulfuric acid certain nitroso compounds and diphenylamine condense through the *para*-position to form highly colored blue quinonimines, sometimes used to detect the presence of a nitroso group<sup>403</sup>.

Safranine, one of the earliest synthetic dyes, is a derivative of phenazine. A safranine dye may easily be obtained by heating *p*-nitroso-*N,N*-dimethylaniline with a primary aromatic amine in the presence of its hydrochloride<sup>404</sup>.

Hydroxylamine will transform an aromatic nitroso compound into a diazonium hydroxide<sup>400,405</sup>. The reaction is probably catalyzed by base and is limited to those nitroso derivatives which may not isomerize into oximes. As expected, many nitrosopyrroles and nitrosophenols do not react in this way with hydroxylamine<sup>406</sup>. On the other hand primary and secondary amino derivatives of aromatic nitroso compounds are more resistant to isomerization and are often diazotized by hydroxylamine. The transformation of *p*-anilinonitrosobenzene into *p*-anilinophenyl azide also demonstrates that an initially formed diazonium hydroxide may react further with hydroxylamine to form an azide<sup>407</sup> (equation 230).

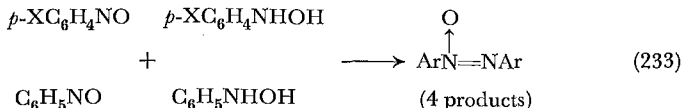
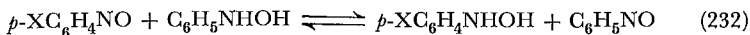


In the presence of hydroxylamine,  $\beta$ -nitroperfluoronitrosoethane is transformed into nitrodifluoroacetic acid<sup>408</sup> (equation 231), apparently by way of an intermediate diazonium compound.

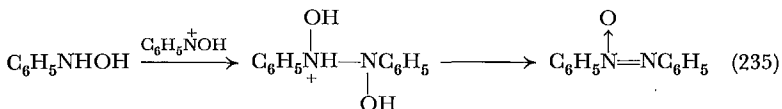
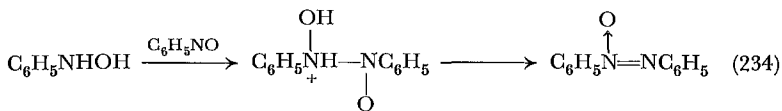


A condensation between an aromatic hydroxylamine and an aromatic nitroso compound leads to (an) azoxy compound(s) and may occur in acidic, neutral or basic solutions. From either *p*-chlorophenylhydroxylamine and nitrosobenzene or *p*-chloronitrosobenzene and phenylhydroxylamine, a mixture of all possible (four)-symmetrically and unsymmetrically substituted azoxybenzenes are formed<sup>409</sup> (equations 232, 233). Apparently an equilibrium between each nitroso and hydroxylamino compound is present. In the

condensation between nitrosobenzene and phenylhydroxylamine in



acid or neutral media, the rate is proportional to the concentration of each reactant and shows a variation with acid concentration. Two mechanisms proposed to fit the data<sup>409</sup> require (1) a reaction between free hydroxylamine and free nitrosobenzene in neutral media (equation 234) and (2) a condensation between phenylhydroxylamine and protonated nitrosobenzene in acidic media (equation 235). Either intermediate accounts for the rapid equilibration between

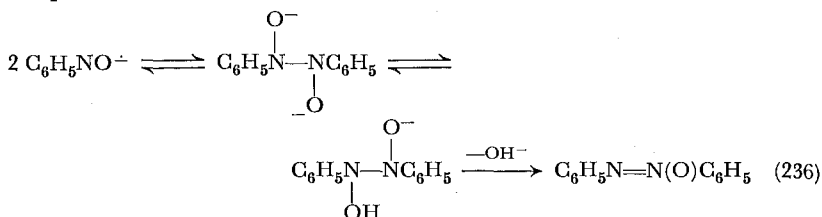


substituted and unsubstituted nitroso and hydroxylamino compounds (equation 232) and for the loss of one-half of the isotope when one reactant<sup>410</sup> is labeled with O<sup>18</sup>. Each is consistent with the requirement for an intermediate with equivalent nitrogen atoms as demonstrated<sup>411</sup> with the condensation between phenylhydroxylamine and nitrosobenzene containing N<sup>15</sup>. In the latter example, azoxybenzene was monobrominated and reductively cleaved with the result that half of the isotope was found in aniline and half in *p*-bromoaniline.

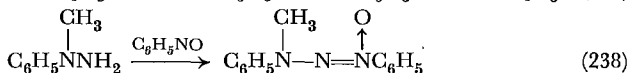
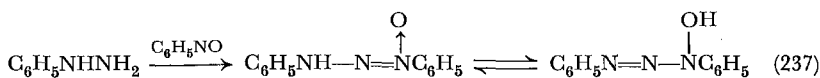
Activation energies for corresponding condensations in acid or neutral media of nitrosobenzene with aniline ( $E_a$  5.83 kcal/mole) and phenylhydroxylamine ( $E_a$  10.8 kcal/mole) and activation entropies ( $\Delta S^\ddagger$  -55.6 cal deg<sup>-1</sup> mole<sup>-1</sup> for aniline and  $\Delta S^\ddagger$  -32.5 cal deg<sup>-1</sup> mole<sup>-1</sup> (estimated) for phenylhydroxylamine) reveal a higher order of reactivity for the aniline-nitrosobenzene reaction in agreement with a greater basicity of aniline over phenylhydroxylamine [ $pK_a$  5.804 for protonated aniline and 3.462 for protonated phenylhydroxylamine in methanol<sup>394</sup> at 25°].

In the presence of certain bases nitrosobenzene and phenylhydroxylamine rapidly produce quantitatively nitrosobenzene anion

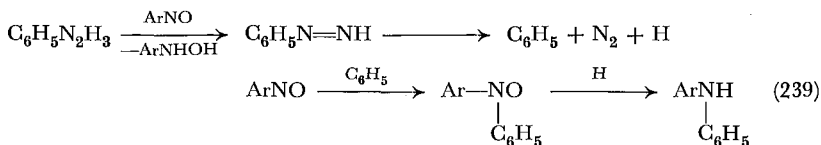
radicals detected by esr. Second-order kinetics for the decay of the radical anions is consistent with the following rapid equilibrium for the condensation in basic solution<sup>284</sup> (equation 236). It is particularly interesting that the nitrosobenzene radical anion is slowly formed in a solution of azoxybenzene in dimethyl sulfoxide 50 % saturated with potassium hydroxide<sup>284</sup>.



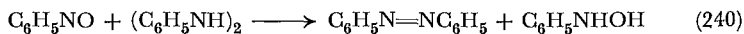
Apparently an expected adduct is readily formed on mixing a monosubstituted or an unsymmetrically disubstituted hydrazine with an aromatic nitroso compound. Dehydration to a triazene either does not occur or is insignificant and the predominant reaction for the intermediate is an oxidation to a triazene-*N*-oxide<sup>412, 413, 414</sup> (equations 237, 238). A diarylamine is also produced in certain



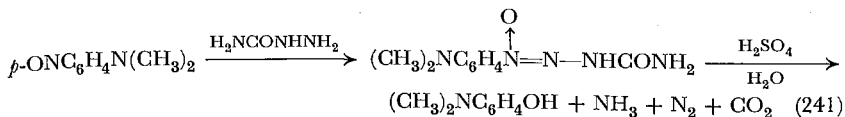
condensations between an arylhydrazine and an aromatic nitroso compound. From isotope labeling it has been shown that the amine nitrogen is generated from the nitroso group<sup>415</sup>. A possible explanation would require dehydrogenation to phenyldiimide and its decomposition to phenyl radicals. A diaryl nitroxide, produced by the combination of nitrosobenzene and phenyl, would then be reduced to a corresponding diaryl amine (equation 239). In support



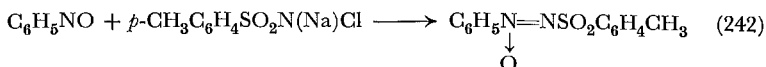
of the step requiring dehydrogenation, it is known that nitrosobenzene combines with hydrazobenzene to give azobenzene and phenylhydroxylamine<sup>416</sup> (equation 240).



Semicarbazide combines with *p*-nitrosodimethylaniline to give the expected triazene-*N*-oxide<sup>417</sup> (equation 241) which is transformed into *p*-dimethylaminophenol on hydrolysis.

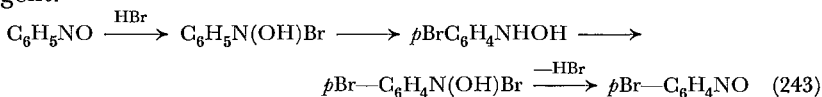


On mild heating in pyridine, chloramine-T reacts with nitrosobenzene to form an azoxysulfone<sup>418</sup> (equation 242) and may proceed either with the formation of an intermediate nitrene or by an addition and elimination sequence<sup>419</sup>.



### T. Substitution Reactions in Aromatic Nitroso Compounds

Substitution reactions of nitrosobenzene are unknown. Bromination<sup>349</sup> and nitration<sup>420</sup>, which give *p*-bromo- and *p*-nitronitrosobenzene respectively, do not require ring-activation through electron release from the nitroso group since they may proceed with the formation of intermediate hydroxylamine derivatives. An explanation for the catalysis of the bromination reaction by hydrogen bromide requires the initial formation of *N*-bromophenylhydroxylamine<sup>349</sup> (equation 243). In the absence of more definitive information a similar explanation based on the intermediacy of a phenylhydroxylamine derivative in the nitration reaction should be questioned. The reaction is carried out in carbon tetrachloride containing phosphorous pentoxide with dinitrogen pentoxide as the nitrating agent.



As an activator in nucleophilic displacement reactions of certain aromatic compounds, the nitroso group is more effective than the nitro group. In boiling sodium hydroxide solution 2,4-dinitrodimethylaniline is barely attacked whereas *p*-nitrosodimethylaniline is hydrolyzed to give nearly quantitative yields of dimethylamine and quinone monoxime<sup>249</sup>. Extension of this reaction to other *p*-nitroso-*N,N*-dialkylanilines provides an important preparative method for pure secondary amines. Displacement of the alkoxy

group in an alkyl ether of *p*-nitrosophenol may occur in a similar manner on treating the ether with a primary aromatic amine in the presence of acid<sup>421</sup> (equation 243a) but *p*-nitrosophenol undergoes more complex changes. In the presence of aniline, it is transformed



into *p*-hydroxyazobenzene in acetic acid medium, into azophenine (cf. equation 229) in hydrochloric acid and into an indoaniline in strong sulfuric acid. A greater reactivity of *p*-bromonitrosobenzene in comparison with *p*-bromonitrobenzene toward silver nitrate has been described also as an illustration of the electron withdrawing power of the nitroso group<sup>249</sup>.

Dipole moments and base-strengths provide additional evidence of the electron-withdrawing capacity of the nitroso group. The dipole moment of 3.2 D for nitrosobenzene is reduced to 0.84 D for *p*-nitronitrosobenzene<sup>422</sup>. The large value of 6.9 D for *p*-nitrosodimethylaniline which exceeds the vector sum, 4.8 D, of the moments of dimethylaniline and nitrosobenzene has been ascribed to a contribution from a zwitterionic structure, cf. IIIC, where the zwitterion itself would be expected to have a dipole moment in the order of 30 D<sup>423</sup>.

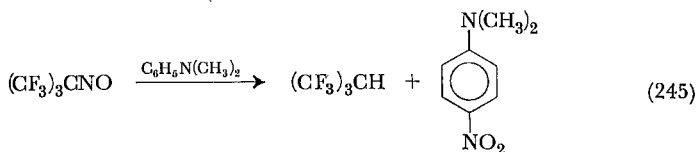
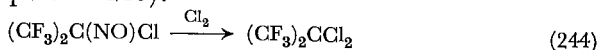
The zwitterionic structure for *p*-nitrosodimethylaniline may account for its otherwise unpredictably high base strength ( $pK_a$  4.0)<sup>424</sup> which is about one  $pK$  unit lower than that of *N,N*-dimethylaniline ( $pK_a$  5.15)<sup>425</sup>. In marked contrast *p*-nitroaniline ( $pK_a$  1.11) is a weaker base than aniline ( $pK_a$  4.62)<sup>425</sup> by over three  $pK$  units<sup>426,427</sup>.

Resonance between the nitroso group and an attached aromatic ring would be reflected in a shortening of the C-nitroso bond. In *p*-iodonitrosobenzene this has been demonstrated in a C-nitroso bond of 1.28 Å appreciably shorter than the C—N bond of 1.49 Å in aliphatic amines<sup>428</sup>.

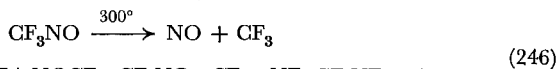
## U. Cleavage of C-Nitroso Bond

It has been suggested that initial nitrosation at carbon is reversible in nitrosative decarboxylation (equation 35) and that mineral acid may replace the nitroso group in a nitrosotoluene with hydrogen (equation 203). There are several other reactions in which cleavage of the C-nitroso bond occurs readily. Geminal dihalides may be prepared from corresponding nitrosochlorides and chlorine<sup>118</sup> (equation 244). At room temperature dimethylaniline in ether

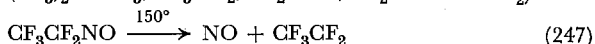
replaces the nitroso group in perfluoro 2-nitroso-2-methylpropane with hydrogen<sup>118</sup> (equation 245).



Pyrolysis of trifluoronitrosomethane and of pentafluoronitrosoethane has been assumed to proceed with initial cleavage of the C-nitroso bond<sup>429</sup> (equations 246, 247). It should be noted that a

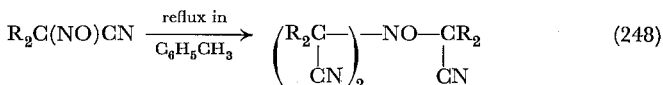


(Products isolated:  $(\text{CF}_3)_2\text{NOCF}_3$ ,  $\text{CF}_3\text{NO}_2$ ,  $\text{CF}_2=\text{NF}$ ,  $\text{CF}_2\text{NF}$  and  $\text{COF}_2$ )

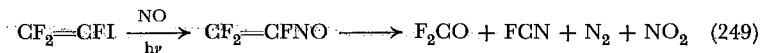


(Products isolated:  $\text{CF}_3\text{NO}_2$ ,  $\text{CF}_3\text{N}=\text{NCF}_3$ ,  $(\text{CF}_3)_2\text{NF}$ ,  $\text{CF}_4$ ,  $\text{COF}_2$  and nitrogen oxides)

molecular rearrangement is apparently required for the formation of the product, hexafluorodimethylamine, in the latter reaction. A similar cleavage in the mass spectrometer leads to the formation of the nitrosyl cation ( $\text{NO}^+$ )<sup>429</sup>. Pyrolysis of geminal nitrosocyanides also proceeds with initial cleavage of the C-nitroso bond<sup>430</sup> (equation 248).



The reversible photochemical dimerization of perfluoronitrosoalkanes cf. III.A, provides a classical example of the photolytic cleavage of the C-nitroso bond. In another example it is presumed that perfluoronitrosoethylene is initially formed in the irradiated mixture of perfluoroiodoethylene and nitric oxide which gives decomposition products<sup>431</sup> (equation 249). Irradiation of nitrosyl cyanide brings about dissociation into nitric oxide and cyanogen radicals<sup>432</sup>. Further discussion of the photolytic cleavage of the C-nitroso bond is presented in Chapter 4.

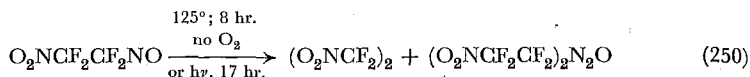


## V. Pyrolytic and Photolytic Disproportionations

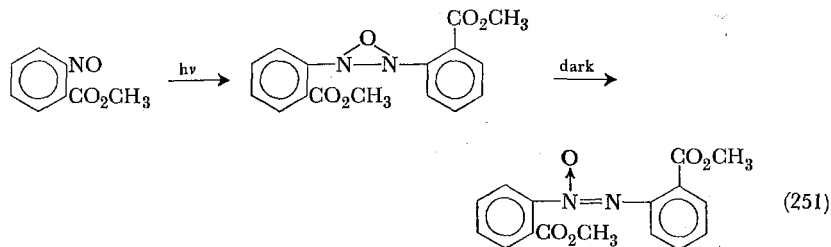
Bamberger first proposed that nitroso compounds may disproportionate with the simultaneous formation of a hydroxylamine and

a nitro compound. On this basis he explained the formation of azoxybenzene, nitobenzene, aniline, *o*-hydroxyazobenzene, *o*-hydroxyazoxybenzene, hydroquinone, *p*-hydroxyazoxybenzene and other products on exposing nitrosobenzene in benzene to sunlight. The same reaction(s) occur(s) more slowly in the dark or on heating nitrosobenzene in petroleum ether<sup>433</sup>.

Disproportionation may lead directly to the formation of an azoxy and a nitro compound, the products obtained from both pyrolysis and photolysis of  $\beta$ -nitroperfluoronitrosoethane<sup>434</sup> (equation 250). Photolysis transforms methyl *o*-nitrosobenzoate into the correspond-



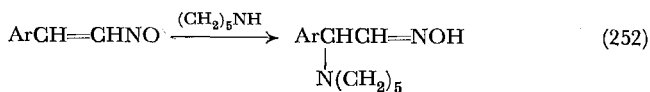
ing azoxy compound through an intermediate claimed to be the three-membered ring isomer of the azoxy compound<sup>182</sup> (equation 251). Methyl nitrobenzoate was not reported.



## W. Miscellaneous Reactions of Nitroso Compounds

### 1. Conjugate addition

Piperidine adds in the 1,4-manner to  $\alpha,\beta$ -unsaturated nitrosoalkenes<sup>435</sup> (equation 252).

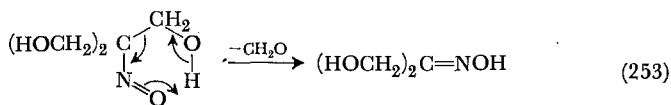


### 2. Fragmentation

On formation trihydroxymethylnitrosomethane dissociates into the oxime of dihydroxyacetone and formaldehyde<sup>129</sup>. An appealing explanation calls for a redistribution of electrons in a cyclic transition state (equation 253) from which formaldehyde is eliminated. The

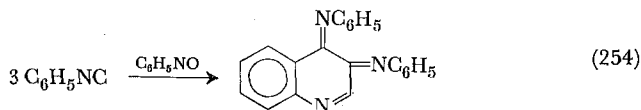


reaction is reminiscent of decarboxylation of  $\alpha$ -nitrosocarboxylic acids, cf. II.J.

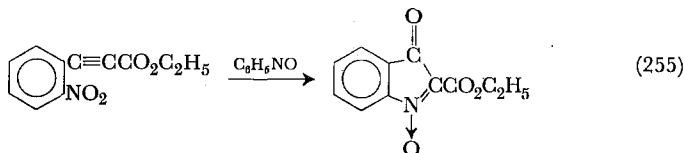


### 3. Reactions promoted by the presence of nitrosobenzene

Trimerization of phenyl isocyanide gives the dianil of 1-aza-3,4-naphthoquinone<sup>436</sup> (equation 254).



In the presence of nitrosobenzene, ethyl *o*-nitrophenylpropiolate undergoes isomerization with ring-closure<sup>437</sup> (equation 255).



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# Methods of formation of the nitro group in aliphatic and alicyclic systems

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I. INTRODUCTION.	302
II. THE CONVERSION OF OXIMES TO NITRO COMPOUNDS	302
A. Hydrogenolysis of <i>gem</i> -Dinitro Compounds	302
B. Reduction of Bromonitro Compounds	304
C. Oxidation of Oximes	306
III. THE OXIDATION OF AMINES	308
A. Peracids	308
B. Potassium Permanganate	310
IV. THE REACTION OF ACTIVE METHYLENE GROUPS WITH NITRATING AGENTS	310
A. Alkyl Nitrates	310
B. Nitric Acid.	314
C. Acetone Cyanohydrin Nitrate	315
V. THE NITRATION OF CARBON-CARBON DOUBLE BONDS	316
A. Acetyl Nitrate	316
B. Nitryl Chloride	318
C. Dinitrogen Tetroxide	319
D. Dinitrogen Trioxide	320
E. Nitrosyl Chloride	323
F. Nitric Acid.	323
VI. DISPLACEMENT REACTIONS BY NITRITE IONS	325
A. Silver Nitrite	325
1. General nature of the reaction	325
2. Stereochemistry and mechanism.	325
3. Synthesis	326
4. Experimental conditions	328
B. Alkali Metal Nitrites	329
1. General nature of the reaction	329
2. Mechanism	330

3. Synthesis . . . . .	332
4. Experimental conditions . . . . .	334
VII. POLY-NITRO COMPOUNDS . . . . .	334
A. ter Meer Reaction . . . . .	335
B. Kaplan-Shechter Reaction . . . . .	336
1. General nature of the reaction . . . . .	336
2. Mechanism . . . . .	336
3. Synthesis. . . . .	338
4. Experimental conditions . . . . .	339
C. Oxidation of Pseudonitroles . . . . .	339
D. Other Methods . . . . .	339
VIII. MISCELLANEOUS METHODS . . . . .	340
IX. REFERENCES . . . . .	342

## I. INTRODUCTION

The vapor phase nitration of saturated aliphatic hydrocarbons was discovered by H. B. Hass<sup>1</sup> in 1934, and the preparation of nitromethane, nitroethane, both nitropropanes, and the four nitrobutanes from hydrocarbons was described<sup>2</sup>. The invention of vapor phase nitration was followed by reports on the nitration of *n*-pentane<sup>3</sup>, *i*-pentane<sup>4</sup>, ethane<sup>5</sup>, and methane<sup>6</sup>. The waste of natural gas in the oil fields inspired Hass to find new reactions of these simple unreactive hydrocarbons, and he created a new industry. Modifications in the process were reported<sup>7,8</sup> and the nitration studies were expanded<sup>9-12</sup>. These findings have been summarized by Hass and Shechter<sup>13</sup>.

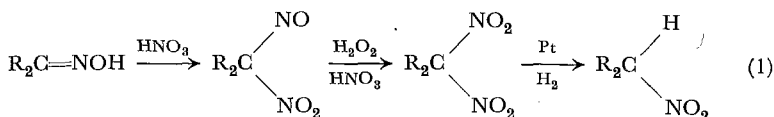
The vapor phase nitration of aliphatic hydrocarbons gave tremendous impetus to the study of aliphatic nitro compounds. A mechanism which accounts for the formation of complex mixtures of nitroalkanes by the nitration process has been published by G. B. Bachman<sup>14</sup>. Limitations of the industrial process required the development of synthetic methods for new nitro compounds in quantities needed for research. Methods for the synthesis of aliphatic and alicyclic nitro compounds have been reviewed recently<sup>15</sup>.

## II. THE CONVERSION OF OXIMES TO NITRO COMPOUNDS

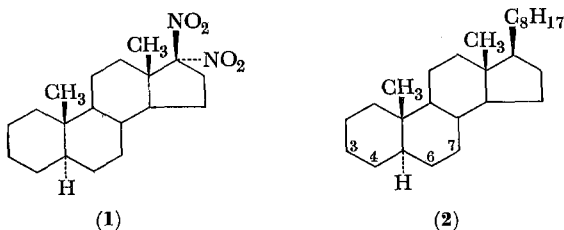
### A. Hydrogenolysis of *gem*-Dinitro Compounds

Usual methods for the synthesis of nitro compounds proved to be unsatisfactory for the preparation of nitro steroids, and a new general

method was developed by Bull, Jones, and Meakins<sup>16</sup>. Nitration of an oxime leads to a pseudonitrole<sup>17</sup> which is easily oxidized to a *gem*-dinitro compound. Controlled reduction with hydrogen and a platinum catalyst affords the mononitro steroid (equation 1).

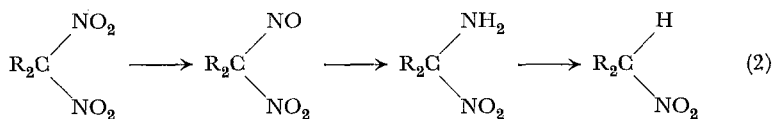


Quantitative hydrogenation of **1** forms 17 $\beta$ -nitro-5 $\alpha$ -androstane, and the overall yield from the oxime to the mononitro compound is 45 %. The stereospecificity of the C—N cleavage is remarkable.



Reduction of the *gem*-dinitro compounds derived from **2** (positions 4, 6, and 7) occurs stereoselectively. The  $\beta$ -nitro derivative is formed exclusively from the 4 and 6 *gem*-dinitro compounds because of protection provided by the angular methyl groups. Controlled hydrogenations of 7,7-dinitro-5 $\alpha$ -cholestane give the 7 $\alpha$ -nitro steroid in a yield of 80 %. Reduction of the 3,3-dinitro compound yields a mixture of both mononitro epimers in equal amounts. Preparation of the more stable isomer of the nitro steroids is illustrated by epimerization of 4 $\beta$ -nitro-5 $\alpha$ -cholestane with sodium bicarbonate to 4 $\alpha$ -nitro-5 $\alpha$ -cholestane, the equatorial isomer, in a 90 % yield.

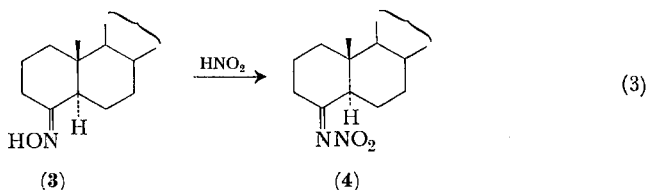
Intermediates in the reduction are not isolated, but the requirement of four moles of hydrogen permits a reasonable representation for the conversion (equation 2).



There are two secondary reactions that may reduce the overall yield in the synthetic sequence<sup>16</sup>. Oximes are converted to ketones by nitrous acid<sup>18</sup>, and nitrous acid also produces nitrimines<sup>19,20</sup>, illustrated by the conversion of **3** to **4** (equation 3). Both unwanted



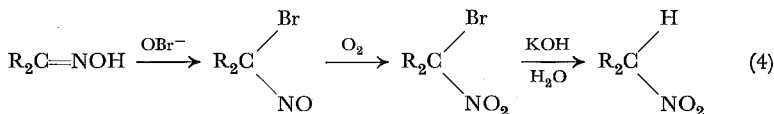
reactions can be minimized by the use of carefully purified nitric



acid.

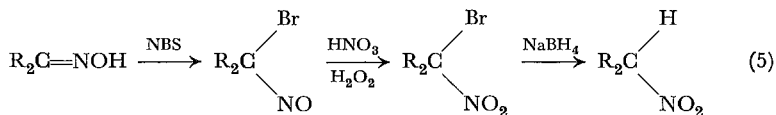
### B. Reduction of Bromonitro Compounds

Forster described the quantitative conversion of camphor oxime to 2-bromo-2-nitrobornane<sup>21</sup>. On treatment with hypobromite, the oxime is converted to a bromonitroso compound which is readily oxidized by air to 2-bromo-2-nitrobornane. The bromonitro compound is reduced to 2-nitrobornane with aqueous potassium hydroxide<sup>22</sup> (equation 4). The procedure is satisfactory and has been



used by several investigators for studying the reactions of 2-bromo-2-nitrobornane<sup>23</sup>, although a realistic overall yield is 32 %<sup>24</sup>.

However, Forster's sequence of reactions is not a general method<sup>25</sup>. Iffland and Criner<sup>26</sup> report substantial modifications which provide a more useful method. In aqueous sodium bicarbonate a ketoxime reacts with *N*-bromosuccinimide to form a bromonitroso compound which is oxidized by a solution of nitric acid and hydrogen peroxide to a bromonitro compound. Sodium borohydride in methanol reduces the bromonitro compound; a high mole ratio of borohydride to bromonitro compound is important (equation 5). Iffland and Yen<sup>27</sup> report the synthesis of ten secondary nitroalkanes



from aliphatic ketoximes in yields that vary from 10 to 48 % (Table 1). The experimental procedure is simplified by not isolating or purifying the intermediate bromonitroso product or the bromonitro compound. Difficulties in the purification of the final product are

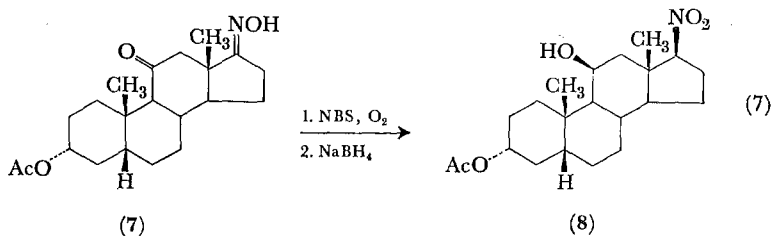
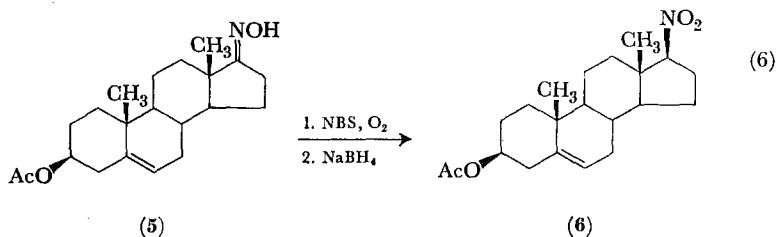
TABLE 1. Conversion of ketoximes to nitro compounds<sup>26,27</sup>.

Ketoxime	Bromonitro compound		Yield, %
	Yield, %	Product of reduction	
Cyclobutanone	69	Nitrocyclobutane	33
Cyclopentanone	72	Nitrocyclopentane	76
Cyclohexanone	63	Nitrocyclohexane	80
Cycloheptanone	38	Nitrocycloheptane	76
Pinacolone		3-Nitro-2,2-dimethylbutane	30 <sup>a</sup>
3-Methyl 2-butanone		3-Nitro-2-methylbutane	48 <sup>a</sup>

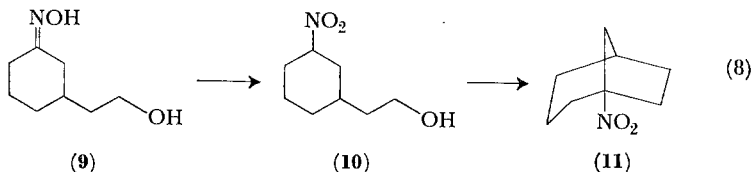
<sup>a</sup> Overall yield from oxime.

thereby largely eliminated. The *N*-bromosuccinimide may be replaced by *N*-bromoacetamide. A solvent system composed of dioxane and water is advantageous in the bromination of pinacolone oxime.

The synthetic method developed by Iffland is useful for the synthesis of nitrocycloalkanes and secondary aliphatic nitro compounds, especially if the carbon chain is branched. With some modification the procedure is applicable to the preparation of nitro steroids. Patchett<sup>28</sup> has found that air oxidation of the bromonitroso intermediate is better than a mixture of nitric acid and hydrogen peroxide. For instance, the conversion of oxime **5** to **6** is achieved in a yield of 55 % without the isolation of any intermediate (equation 6). Similarly, oxime **7** is converted to **8** in 30 % yield (equation 7). The success of Iffland's method in the presence of other functional groups



is noteworthy, and another example is the conversion of **9** to the nitro alcohol **10**. The tosylate of the nitro alcohol reacts with sodium hydride in dimethylformamide to form the bicyclic product **11** with a bridgehead nitro group<sup>29</sup> (equation 8).

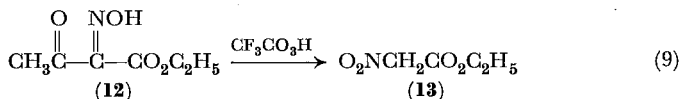


But Iffland's method is not applicable to aldoximes and aromatic ketoximes<sup>25</sup>. Also the method failed in the case of 3-hydroxyimino-5 $\alpha$ -cholestane. The major product is the parent ketone and only small amounts of the expected bromonitroso and bromonitro compounds<sup>16</sup> are obtained.

### C. Oxidation of Oximes

Peroxytrifluoroacetic acid, a reagent developed by Emmons and Pagano<sup>30</sup>, is the first useful reagent to oxidize oximes directly to nitro compounds. An earlier report on the oxidation of oximes is of little value<sup>31</sup>.

The simplicity and brevity of the experimental procedure are attractive features of the method. Peroxytrifluoroacetic acid in acetonitrile is added to a solution of the oxime in acetonitrile at reflux temperature. A buffer is necessary to neutralize the trifluoroacetic acid formed in the reaction. With aliphatic oximes sodium bicarbonate is satisfactory, and with aromatic and alicyclic oximes disodium hydrogen phosphate is effective. A small amount of urea is used to scavenge oxides of nitrogen. Trifluoroacetic acid and chloroform are other solvents for the reaction. The effectiveness of peroxytrifluoroacetic acid in the oxidation of oximes to nitro compounds is evident from the data given in Table 2. The oxidation of  $\alpha$ -oximinoacetoacetic ester (**12**) is accompanied by cleavage to ethyl nitroacetate (**13**) in a yield of 40% (equation 9). Sodium dichromate in



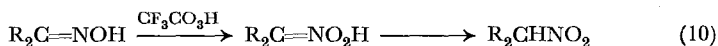
acetic acid oxidizes  $\alpha$ -oximinoacetoacetic ester to ethyl nitroacetate<sup>32</sup>

TABLE 2. Oxidation of oximes with peroxytrifluoroacetic acid<sup>30</sup>.

Product from corresponding oxime	Yield %
Nitrocyclopentane	60
Nitrocyclohexane	62
Nitrocycloheptane	51
1-Nitrooctane	63
1-Nitroheptane	72
2-Nitrobutane	47
2-Nitro-3-methylbutane	49
$\alpha$ -Phenylnitroethane	69
$\omega$ -Nitroacetophenone	76
Diethyl nitromalonate	66
1-Cyclopropylnitroethane	42
Dicyclopropylnitromethane	35

in a yield of 61%. Large quantities of  $\omega$ -nitroacetophenone are easily prepared according to the excellent procedure of Long and Troutman<sup>33</sup>. Nitromethane and benzaldehyde are condensed by sodium hydroxide in methanol to 1-phenyl-2-nitroethanol which is oxidized in a mixture of aqueous acetic acid and potassium dichromate. The overall yield is 62%.

Emmons suggests that the oxime is oxidized to the nitronic acid which isomerizes to the stable product and that acetonitrile is a superior solvent because it facilitates the tautomerization (equation 10).



The oximes of pinacolone and trimethylacetaldehyde are not oxidized by peroxytrifluoroacetic acid, the oxidation being impeded by steric hindrance<sup>30</sup>. The oxidation of 3-hydroxyimino-5 $\alpha$ -cholestane with peroxytrifluoroacetic acid or with peracetic acid was not successful<sup>16</sup>. In exploratory experiments for the preparation of 17-nitro steroids from the corresponding oximes, a product which was difficult to purify formed, although the presence of a nitro group in the crude product was detected by infrared spectroscopy<sup>28</sup>. It should be noted that peroxytrifluoroacetic acid is a useful reagent for the oxidation of a carbon-carbon double bond to an oxirane<sup>34</sup>, and the experimental procedure is similar to that for the oxidation of oximes. Apparently the product from the oxidation of an unsaturated oxime with peroxytrifluoroacetic acid has not been determined.

Peroxytrifluoroacetic acid is prepared in acetonitrile by the reaction of trifluoroacetic anhydride and 90 % hydrogen peroxide, which is commercially available. The hazards of 90 % hydrogen peroxide have been described<sup>35</sup>.

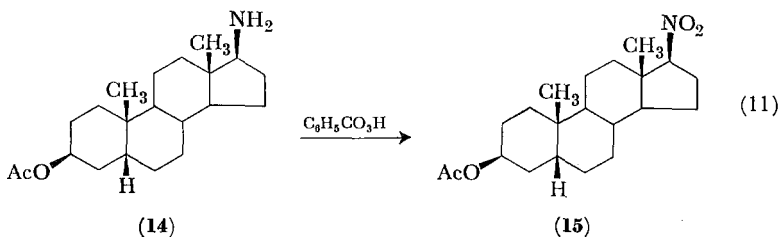
### III. THE OXIDATION OF AMINES

#### A. Peracids

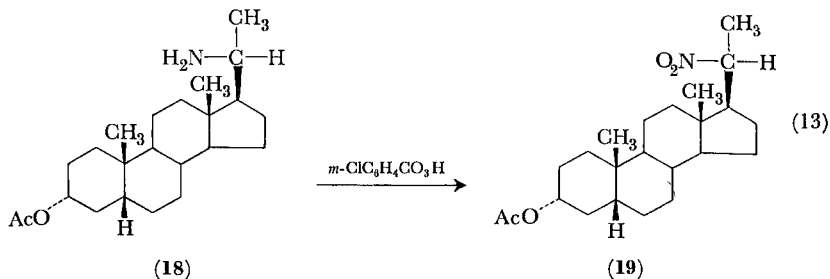
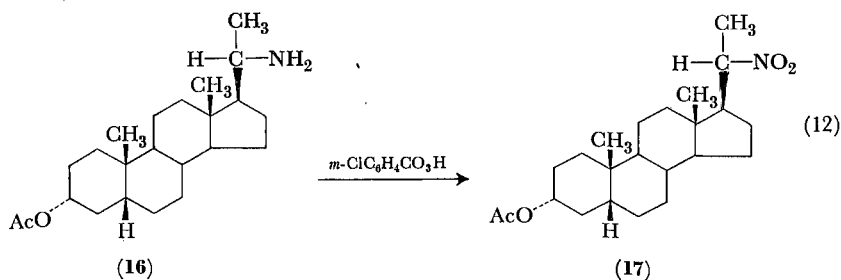
The earliest attempts to prepare aliphatic nitro compounds by the oxidation of amines did not lead to a useful method<sup>36</sup>, but Emmons reports the successful conversion of aliphatic amines to nitroalkanes with peracetic acid<sup>37</sup>. Tertiary nitrooctane, nitrocyclohexane, 2-nitrobutane, and 1-nitrohexane are obtained in yields of 87, 70, 65, and 32 %, respectively, from the corresponding amines.

Oxidation of amines does not occur when peroxytrifluoroacetic acid is used as the oxidant. Instead the amine is protonated by the trifluoroacetic acid present in the peracid. Acylation prevails when a buffer system is used. The product, in this case, is the N-alkyl-trifluoroacetamide.

Perbenzoic acid<sup>38</sup> in benzene at 75° oxidizes 3 $\beta$ -acetoxy-17 $\beta$ -amino-5 $\beta$ -androstane (**14**) to 3 $\beta$ -acetoxy-17 $\beta$ -nitro-5 $\beta$ -androstane (**15**) (equation 11). The 5 $\alpha$ -isomer is oxidized successfully also.

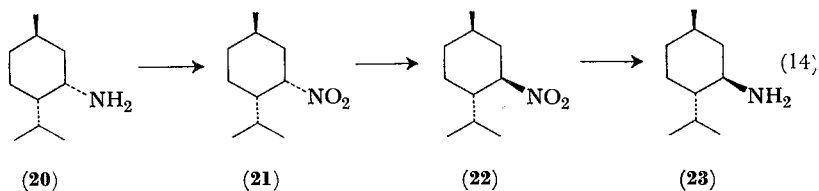


The oxidation of steroidal amines to nitro steroids by *m*-chloroperbenzoic acid<sup>39</sup> is a valuable modification of the method devised by Emmons. The stability and commercial availability of *m*-chloroperbenzoic acid will enhance the use of this method. The steroidal amine **16** is oxidized to the nitro steroid **17** in 50 % yield (equation 12). Similarly, the epimeric amine **18** is converted to **19** in 79 % yield (equation 13). Retention of the stereochemical configuration at C-20 is striking, and in general the yields are reported to be high. A large mole ratio of oxidant to amine is necessary to suppress the



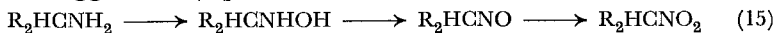
formation of nitroso dimers. Oxidations of  $3\alpha$ - and  $3\beta$ -steroidal amines to the corresponding nitro compounds are also recorded.

The oxidation of neomenthylamine (**20**) to 3-nitro-*p*-menthane (**21**) by peracetic acid without racemization is reported<sup>40</sup>. Epimerization of **21** to **22** occurs with sodium bicarbonate, and the nitro compound **22** is reduced with iron powder in acetic acid without racemization<sup>41</sup> to the amine **23**. The sequence of reactions provides



a route for the epimerization of amines and also illustrates the use of peracetic acid in the oxidation of an amine to a nitro compound with retention of configuration at the adjacent asymmetric carbon atom (equation 14).

The mechanism for the oxidative conversion of amines to nitro compounds has not been studied specifically, but a plausible course has been suggested<sup>42</sup> (equation 15). Indeed nitroso dimers have been isolated.<sup>39,43</sup>



The Victor Meyer reaction and the modified Victor Meyer reaction give mixtures of nitro compounds and nitrites (e.g. see section VI.A.1). Oxidation of amines by peracids affords only the nitro compound. Formation of one product facilitates isolation and avoids tedious fractional distillations. The oxidation of amines seems to be limited to those compounds which do not contain other functional groups susceptible to the action of peracids. Carbon-carbon double bonds form epoxides<sup>44</sup>, and carbonyl groups undergo the Baeyer-Villiger oxidation<sup>45</sup> with peracids.

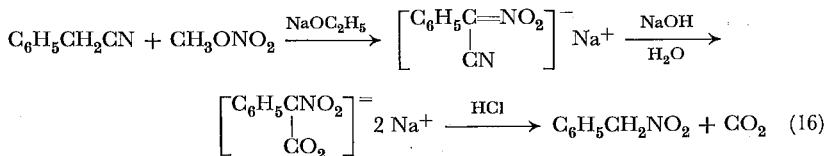
### B. Potassium Permanganate

Tertiary amines are oxidized to the corresponding nitro compounds by potassium permanganate in a solution composed of 80 % acetone and 20 % water to which magnesium sulfate is added<sup>42</sup>. The preparation of seven tertiary nitro compounds in yields ranging from 70 to 83 % is described<sup>42</sup>. The isolation of 1,8-dinitro-*p*-menthane in 61 % yield indicates that diamines could be a source of dinitro compounds with the appropriate oxidizing agent. However, the permanganate oxidation of amines is obviously limited to those compounds that are resistant to the action of a powerful oxidizing agent.

## IV. THE REACTION OF ACTIVE METHYLENE GROUPS WITH NITRATING AGENTS

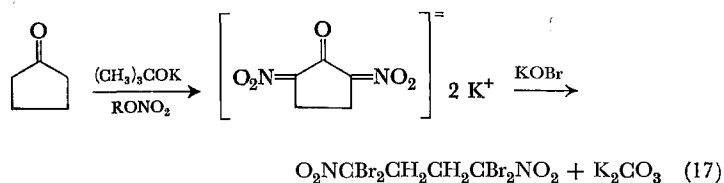
### A. Alkyl Nitrates

The nitration of arylacetonitriles<sup>46</sup> and arylacetic esters<sup>47</sup> by alkyl nitrates was discovered by Wislicenus. The reaction of benzyl cyanide, sodium ethoxide, and methyl nitrate provided a route to phenyl-nitromethane<sup>48</sup> (equation 16). The overall yield was 50–55 %.



Fluorene was converted to 9-nitrofluorene in high yield<sup>49</sup>, and Wieland<sup>50</sup> applied the reaction to the nitration of ketones. Cyclohexanone reacted with potassium ethoxide and ethyl nitrate in a mixture of ethanol and diethyl ether to form a mixture of  $\alpha$ -nitrocyclohexanone and  $\alpha,\alpha'$ -dinitrocyclohexanone.

The procedure by Wieland leads to nitro ketones in low yields<sup>51</sup>, and Feuer and coworkers report a thorough study to determine the optimum experimental conditions: mode of addition of the reagents, reaction time, temperature, solvent, and base. For example, cyclopentanone is treated with excess sublimed potassium *t*-butoxide in tetrahydrofuran at a low temperature ( $-30^\circ$ ) to minimize condensation of the ketone, and amyl nitrate is added. A small amount of alcohol lowers the yield drastically, and a substantial excess of base is essential. A short period of time suffices for the reaction, and the product must be isolated promptly. The yield of the dipotassium salt is determined by bromination with potassium hypobromite to 1,1,4,4-tetrabromo-1,4-dinitrobutane in a 72% overall yield (equation 17). Cyclohexanone, cycloheptanone, and cyclooctanone react



similarly, and the yields of tetrabromodinitroalkanes range from 35 to 72%. Reduction of tetrabromodinitrobutane with sodium borohydride yields 1,4-dinitrobutane<sup>52</sup>.

A superior method by Feuer and Anderson<sup>53</sup> for the synthesis of  $\alpha,\omega$ -dinitroalkanes is found in the cleavage of dinitrocycloalkanones. The potassium salt of 2,6-dinitrocyclohexanone is converted in acidic medium to 1,5-dinitropentane in 78% yield. In a comparable manner, 1,6-dinitrohexane (75%) and 1,4-dinitrobutane (72%) are prepared. The new synthesis of terminal dinitroalkanes is a general reaction for which the requisite cyclic ketones are readily available.

The method developed for the preparation of  $\alpha,\alpha'$ -dinitrocyclic ketones is applicable to aliphatic nitriles,  $\alpha,\omega$ -dinitriles, aliphatic ketones and aryl alkyl ketones<sup>54</sup>. *N,N*-Dialkylamides undergo alkyl nitration, and the products are isolated as their bromo derivatives<sup>55</sup>. Modifications in the procedure of the alkyl nitrate nitration facilitate the synthesis of mononitro ketones<sup>56</sup>. The  $\alpha$ -nitro ketones are susceptible to a cleavage reaction. Cyclooctanone reacts with potassium *t*-butoxide and amyl nitrate to form  $\alpha$ -nitrocyclooctanone and amyl 8-nitrooctanoate. The utility of alkyl nitrate nitration is evident in Table 3.

In the competitive nitration and cleavage reactions, nitration predominates with the  $\text{C}_5$ ,  $\text{C}_6$ , and  $\text{C}_7$ -cyclic ketones, but cleavage

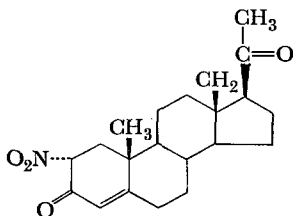


TABLE 3. Alkyl nitrate nitration of ketones<sup>56</sup>.

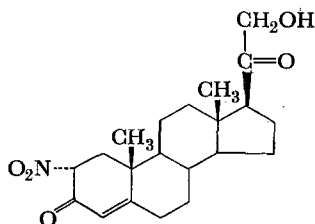
Ketone	Yield of $\alpha$ -nitro ketone %	Yield of $\omega$ -nitrocarboxylic ester %
Cyclopentanone	—	10
Cyclohexanone	20	10
Cycloheptanone	64	4
Cyclooctanone	35	37
Cyclononanone	14	60
Cyclodecanone	14	58
Cyclodoecanone	54	23
2,5-Dimethylcyclopentanone	10	58
2,2,5-Trimethylcyclopentanone	0	53
2,2,4-Trimethylcyclopentanone	82	0
$\alpha$ -Tetralone	59	0
Propiophenone	16	15

dominates with medium ring ketones. Tertiary nitro ketones, which cannot form a stable anion, are cleaved. Dinitration does occur in some instances, and the dinitro ketone and unreacted ketone complicate the isolation of the desired mononitro ketone. Nevertheless, nitration of ketones with alkyl nitrates is the most effective method for the synthesis of  $\alpha$ -nitro ketones.

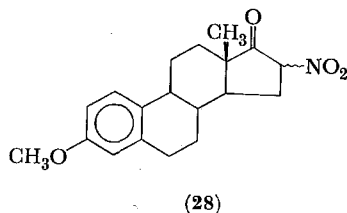
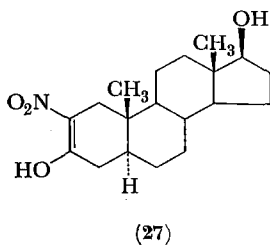
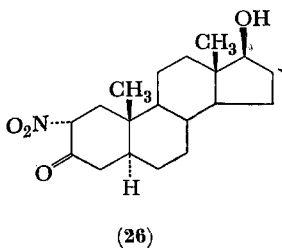
Nitro keto steroids<sup>57</sup> are available by Feuer's method of alkyl nitrate nitration. Treatment of progesterone 20-ethylene ketal and deoxycorticosterone 20-ethylene ketal with potassium *t*-butoxide and amyl nitrate forms the nitro steroids after hydrolysis of the ketals. The yield of 2 $\alpha$ -nitroprogesterone (**24**) is 70%, and the yield of 2 $\alpha$ -nitrodeoxycorticosterone (**25**) is 18%. The presence of a free hydroxyl group appears to interfere seriously with the reaction. Nitration of 17 $\beta$ -tetrahydropyranyloxy-5 $\alpha$ -androstan-3-one and subsequent hydrolysis result in a mixture of the 2 $\alpha$ -nitro ketone **26** and



(24)

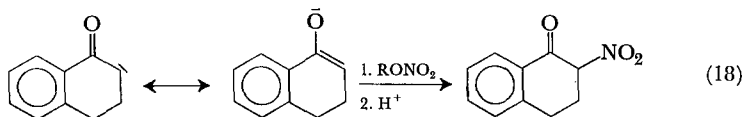


(25)

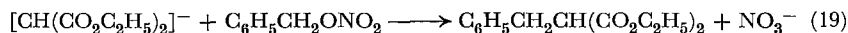


the enol **27**. Nitration of estrone 3-methyl ether gives the nitro ketone **28** in which the 16 $\beta$ - and 16 $\alpha$ -nitro epimers are present in approximately equal amounts. The synthesis of many 2- and 4-nitro ketones is described<sup>57</sup>, and other 16-nitro-17-keto steroids are reported<sup>58</sup>.

Nitration by alkyl nitrates involves nucleophilic displacement by the carbanion on nitrogen of the nitrate ester. The nitro ketone reacts with the base, and acidification is necessary to isolate the



ketone (equation 18). However, with the anion derived from malonic ester or acetoacetic ester displacement on carbon occurs<sup>59</sup> (equation 19).



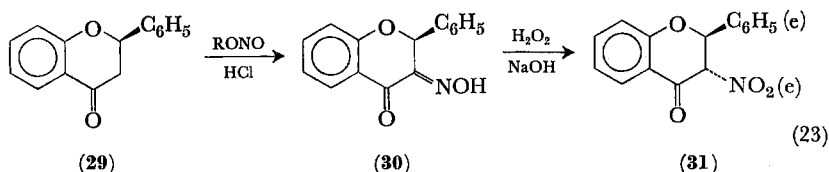
Alkyl nitrates are degraded by bases in three ways: displacement reactions (equation 20),  $\beta$ -elimination reactions (equation 21), and  $\alpha$ -elimination reactions<sup>60</sup> (equation 22). These reactions are largely



avoided at the low temperatures employed in the nitration reaction.

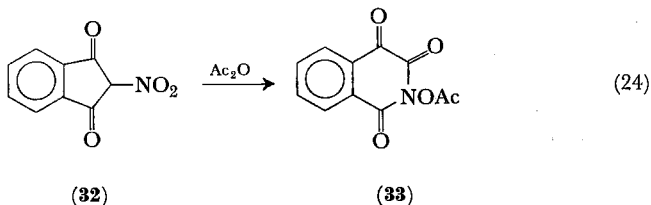
The C-acylation of primary nitroparaffins is noted here in relation to the synthesis of  $\alpha$ -nitro ketones. Benzoyl cyanide and acetyl cyanide react with salts of primary nitroparaffins to form  $\alpha$ -nitro ketones in 30–70 % yields<sup>61</sup>. As a specific example, the lithium salt of 1-nitropropane reacts with benzoyl cyanide to form  $\alpha$ -nitrobutyrophenone in 60 % yield.

Nitro ketones may be prepared by chromic acid oxidation of nitro alcohols<sup>33,62</sup>. The preparation of 3-nitroflavanone (**31**) in 85 % yield by the oxidation of the oxime (**30**) from the flavanone (**29**) with hydrogen peroxide in alkaline solution is reported<sup>63</sup>. Although limited to one example, the method appears to be useful (equation 23).

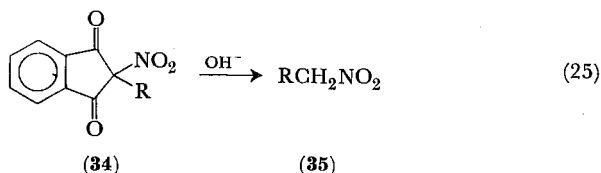


### B. Nitric Acid

The nitration of cyclic  $\beta$ -diketones is accomplished most effectively with nitric acid. For example, indane-1,3-dione is converted to 2-nitroindane-1,3-dione (**32**) in a 78 % yield<sup>64</sup>. The nitro ketone **32** undergoes a novel transformation<sup>65</sup> with acetic anhydride to form the acetate of *N*-hydroxyphthalonimide (**33**) (equation 24). The nitroindanedione synthesis furnishes another method for the preparation of primary nitro compounds. Nitration of the appropriate



indane-1,3-dione forms **34** which is cleaved by dilute aqueous sodium hydroxide to sodium phthalate and the primary nitro compound **35** (equation 25). Thus, 1-naphthylnitromethane<sup>66</sup> may be prepared, as well as other analogs of phenylnitromethane. The preparations of 2-nitro-5,5-dimethylcyclohexane-1,3-dione<sup>67</sup> and 2-nitro-2-carbethoxyindane-1,3-dione<sup>68</sup> are additional illustrations of the nitration of cyclic  $\beta$ -diketones with nitric acid.



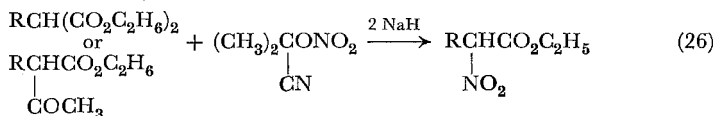
The nitration of 3-bromocamphor with boiling concentrated nitric acid results in a mixture of the corresponding 3-bromo-3-nitro epimers. The mixture is treated with sodium ethoxide, and 3-nitrocamphor<sup>69</sup> is obtained in 17% yield<sup>70</sup>. Obviously few ketones will survive these experimental conditions, but the method provided an  $\alpha$ -nitro ketone<sup>71</sup> for study at a time when these compounds were not readily available.

Nitration of diethyl malonate provides diethyl nitromalonate in 92% yield<sup>72</sup>. Nitration of monoesters of malonic acid with nitric acid affords the  $\alpha, \alpha$ -dinitro esters in low yields<sup>73</sup>.

Diphenylcyanonitromethane<sup>74</sup> is prepared from diphenylcyanomethane and nitrogen dioxide. Diphenylnitromethane is obtained by the action of nitrogen dioxide on diphenylmethane in the presence of copper sulfate and oxygen<sup>75</sup>. Oxides of nitrogen convert diethyl malonate to diethyl oxomalonate and no nitration is observed<sup>76</sup>.

### C. Acetone Cyanohydrin Nitrate

Diethyl nitromalonate is obtained in 45% yield from diethyl malonate, sodium hydride, and acetone cyanohydrin nitrate in tetrahydrofuran.  $\alpha$ -Nitro esters are prepared by the nitration of monosubstituted acetoacetic or malonic esters with acetone cyanohydrin nitrate by the use of excess sodium hydride<sup>77</sup> (equation 26). The yields range from 40 to 70%.



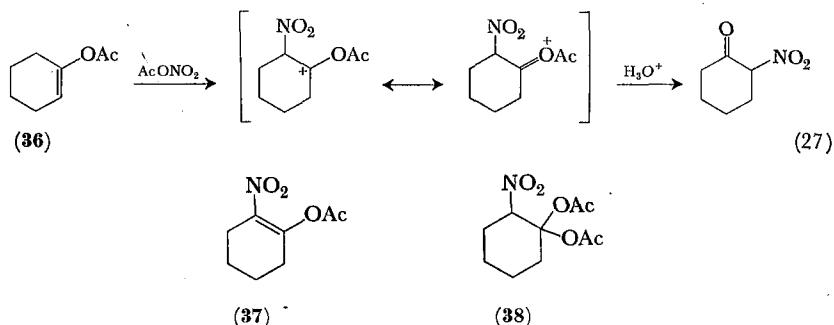
Nitric acid reacts with acetone cyanohydrin in acetic anhydride to form acetone cyanohydrin nitrate in 65–68% yield<sup>78</sup>. Sodium alkoxides destroy the nitration agent<sup>79</sup>. Sodium *n*-amylate reacts with acetone cyanohydrin nitrate to form *n*-amyl nitrate and *n*-amyl  $\alpha$ -hydroxyisobutyrate. Therefore, the choice of base is limited, and sodium hydride is effective. As yet, this nitration method has not found general application.

It should be noted that esters of nitroacetic acid are available by the acidification of the dipotassium salt of nitroacetic acid, which is prepared from nitromethane and potassium hydroxide<sup>80</sup>, and subsequent esterification of the acid<sup>81</sup>. Ethyl nitroacetate is obtained in 60% yield.

## V. THE NITRATION OF CARBON-CARBON DOUBLE BONDS

### A. Acetyl Nitrate

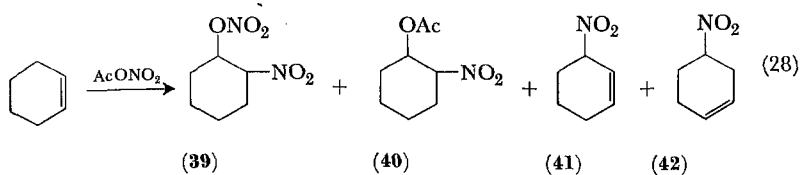
Acetyl nitrate reacts with both enol esters and olefins to produce nitro compounds. The reaction of 2-buten-2-yl acetate with acetyl nitrate<sup>82</sup> yields 3-nitro-2-butanone (13%). Acetyl nitrate and 1-phenyl-1-propen-1-yl acetate react to form  $\alpha$ -nitropropiophenone in 21% yield. Though the initial report indicates that the yields of nitro ketones are low, acetyl nitrate and the enol acetate of cyclohexanone (**36**) react to give 2-nitrocyclohexanone in 40% yield<sup>83</sup> (equation 27). By-products **37** and **38**, which may form, are hydrolyzed to product during the isolation. Although the reaction of



acetyl nitrate and enol esters has not been evaluated completely, the method appears to be convenient and useful.

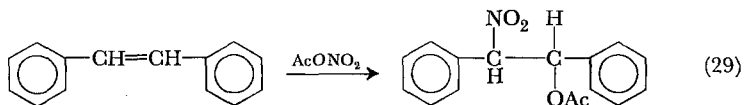
Acetyl nitrate is prepared *in situ* by the reaction of acetic anhydride with nitric acid at 15° according to Bordwell and Garbisch<sup>84</sup>. Careful control of the exothermic reaction is essential, but acetyl nitrate is not formed at lower temperatures. A mole ratio of acetic anhydride to 70% nitric acid of about seven is necessary in order to avoid crystallization of acetic acid at lower temperatures during the nitration. The olefin is introduced at -20° to -30°. The reaction is completed in a brief period of time, and with some olefins acid catalysis is helpful.

Numerous olefins have been studied<sup>84</sup>, and the nitration of cyclohexene<sup>83,84</sup> will suffice as an example (equation 28). The task of

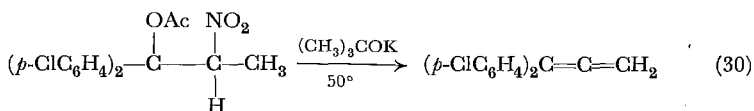


separating four products is formidable. Although **39** and **40** undergo ester exchange in methanol with an acid catalyst, a 30% yield of 2-nitrocyclohexanol is too low to be useful. The reaction of acetyl nitrate with cyclopentene gives products that are analogous to those obtained from cyclohexene. Separation of the complex mixture of products produced in the reaction of acetyl nitrate with olefins poses a serious limitation to the method as a source of nitro compounds.

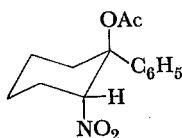
Mainly  $\beta$ -nitro acetates are obtained in the nitration of stilbenes and styrenes<sup>85</sup>. The yield of *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane from the nitration of *trans*-stilbene is 70% (equation 29), and  $\alpha$ -methylstyrene is converted to 1-nitro-2-acetoxy-2-phenylpropane in 70% yield. High yields of  $\beta$ -nitro acetates are also obtained in the reactions of acetyl nitrate with 1,1-diarylethenes<sup>86</sup>. The nitration of



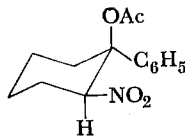
1,1-diphenylethene gives 1-acetoxy-1,1-diphenyl-2-nitroethane in 70% yield.  $\beta$ -Nitro acetates, which are accessible by the nitration reactions, undergo elimination reactions to form allenes, and 1,1-di(*p*-chlorophenyl)allene is prepared in 71% yield from 1-acetoxy-1,1-di(*p*-chlorophenyl)-2-nitropropane by the action of potassium *t*-butoxide (equation 30).



The reaction of acetyl nitrate with 1-phenylcyclohexene<sup>87</sup> results in a mixture of  $\beta$ -nitro acetates in 65% yield. The mixture consists of **43** (75%) and **44** (25%).



(43)



(44)

The preparation of  $\beta$ -nitro acetates, the principal products of the nitration reaction, may be formulated as the result of Markownikoff addition of  $\text{AcO}-\text{NO}_2$ <sup>84</sup> to carbon-carbon double bonds. The reaction is catalyzed by sulfuric acid, which suggests that the nitrating species is  $(\text{AcOHNO}_2)^+$ . Products which are the result of both *cis* and *trans* additions are obtained from a single olefin. In the case of cyclohexene the structures of the numerous products imply the intermediacy of carbonium ions<sup>83</sup>. The addition of acetyl nitrate to 1,1-diarylalkenes yields products which are characteristically derived from carbonium ions. It is suggested that the addition of acetyl nitrate to simple acyclic olefins involves a cyclic transition state<sup>84</sup>.

### B. Nitryl Chloride

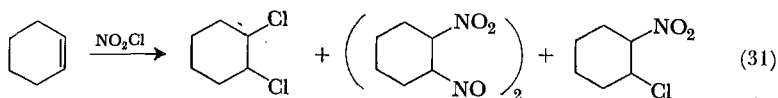
Nitro ketones are obtained by the reaction of nitryl chloride with enol esters<sup>82</sup>. The yields vary considerably, and chlorination may occur. Nitryl chloride appears to be less useful than acetyl nitrate in the conversion of enol esters to nitro compounds. The data are summarized in Table 4.

Nitryl chloride adds to unsymmetrical terminal olefins to yield 1-nitro-2-chloroalkanes<sup>88</sup>. Vinyl bromide and nitryl chloride react to give 1-bromo-1-chloro-2-nitroethane in 85% yield<sup>89</sup>. Nitryl chloride converts cyclohexene<sup>90</sup> to 1,2-dichlorocyclohexane, cyclohexene pseudonitrosite, and 1-chloro-2-nitrocyclohexane (33%)

TABLE 4. Nitration of enol acetates with nitryl chloride<sup>82</sup>.

Enol acetate	Product	Yield %
$(\text{CH}_3)_2\text{C}=\text{CHOCOCH}_3$	$(\text{CH}_3)_2\text{CClCHO}$	21.0
	$(\text{CH}_3)_2\text{CNO}_2\text{CHO}$	12.0
$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{OCOCH}_3$	$\text{CH}_3\text{COCH}(\text{NO}_2)\text{CH}_3$	36.0
$\text{CH}_2=\text{C}(\text{C}_6\text{H}_5)\text{OCOCH}_3$	$\text{C}_6\text{H}_5\text{COCH}_2\text{NO}_2$	36.0
$\text{CH}_3\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{OCOCH}_3$	$\text{C}_6\text{H}_5\text{COCH}(\text{NO}_2)\text{CH}_3$	28.0

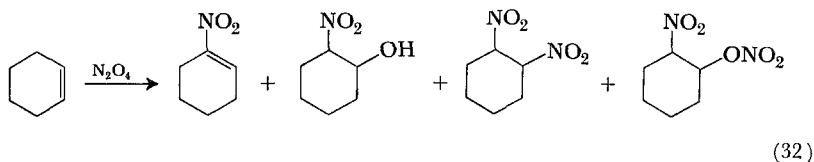
(equation 31).



A mixture which consists of methyl 2,3-dichloropropionate (7%), methyl 2-chloro-3-nitropropionate (75%), and dimethyl 2-chloro-4-nitromethylpentanedioate (5–10%) is obtained from the reaction of nitryl chloride and methyl acrylate at 0°. The suggestion is made that the addition of nitryl chloride to a carbon-carbon double bond is a homolytic process<sup>91</sup> in which nitryl chloride or nitrogen dioxide attacks the terminal position of the double bond, forming a C—N bond exclusively. The intermediate radical reacts with nitryl chloride to form a chloronitro compound or with methyl acrylate and another radical to complete the reaction.

### C. Dinitrogen Tetroxide

The addition of dinitrogen tetroxide to an olefin produces a mixture of nitro compounds<sup>92</sup>. The reactions of ethylene<sup>93</sup>, propylene<sup>94</sup>, isobutylene<sup>95</sup>, and 1-butene<sup>95</sup> with dinitrogen tetroxide are described, and the reaction of cyclohexene with dinitrogen tetroxide at 0° will serve as an illustration<sup>93,96</sup> (equation 32). Ether is used as a solvent, and oxygen is bubbled into the solution. Separation of the mixture is an obvious problem which is complicated by



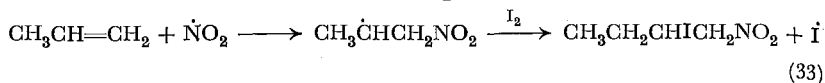
the instability of the products during distillation<sup>93</sup>.

Dinitrogen tetroxide adds to fluoroethylenes to give the corresponding 1,2-dinitroethanes<sup>97</sup>; tetrafluoroethylene yields 1,2-dinitro-1,1,2,2-tetrafluoroethane.

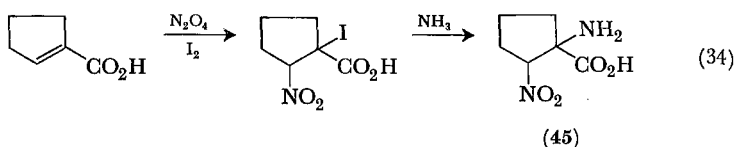
Shechter and Conrad showed that the addition of dinitrogen tetroxide to a carbon-carbon double bond is a free-radical reaction<sup>98</sup>. Dinitrogen tetroxide adds to methyl acrylate to give three distinct products after hydrolysis and neutralization: methyl 3-nitroacrylate (13%), methyl 2-hydroxy-3-nitropropionate (27%), oxalic acid dihydrate (up to 80%), and nitrogen containing polymers of methyl



acrylate. The reaction of dinitrogen tetroxide with olefins in the presence of excess iodine provides additional evidence for the free radical nature of the reaction<sup>99</sup> (equation 33). Iodine traps the



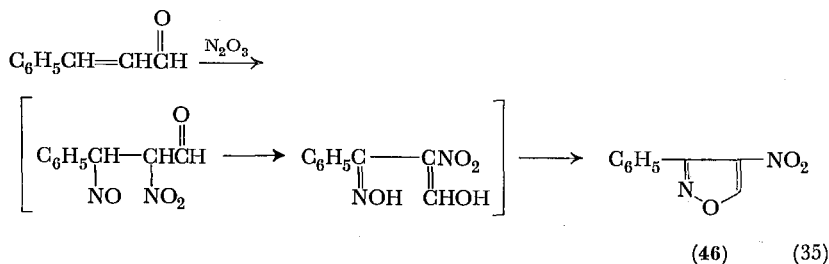
intermediate  $\beta$ -nitroalkyl radical and  $\beta$ -nitroalkyl iodides are obtained in yields that range from 50–70%. Thus, the modification of the nitrogen tetroxide reaction with olefins results in a reaction which is useful for synthesis. Nitro olefins are obtained from the dehydrohalogenation of  $\beta$ -nitroalkyl iodides by sodium acetate. A compound, 1-amino-2-nitrocyclopentanecarboxylic acid (**45**), which is produced by *Aspergillus wentii*, regulates the growth of plants. The nitroamino acid **45** shows novel chemical properties, and the structure is established by synthesis<sup>100</sup> (equation 34).



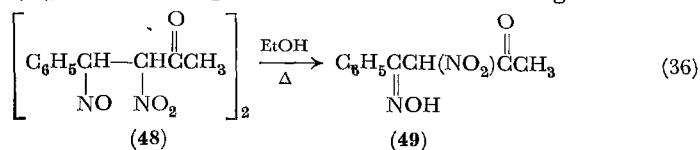
Complex mixtures of products are obtained by the addition of dinitrogen tetroxide to acetylenes<sup>101</sup>. Dinitrogen tetroxide reacts with 3-hexyne to form five products; *cis*- and *trans*-3,4-dinitro-3-hexene (4.5 and 13%, respectively) and 4,4-dinitro-3-hexanone (8%) are the only nitro compounds which were found<sup>101</sup>. The other products are propionic acid (6%) and dipropionyl (16%).

#### D. Dinitrogen Trioxide

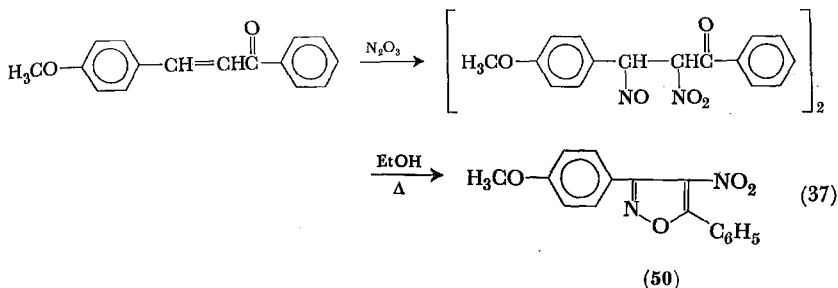
Products containing a nitro group are obtained by the addition of dinitrogen trioxide to carbon-carbon double bonds. Cinnamaldehyde<sup>102</sup> reacts with dinitrogen trioxide to form mainly 4-nitro-3-phenylisoxazole (**46**) (equation 35). Benzalacetone reacts to form a



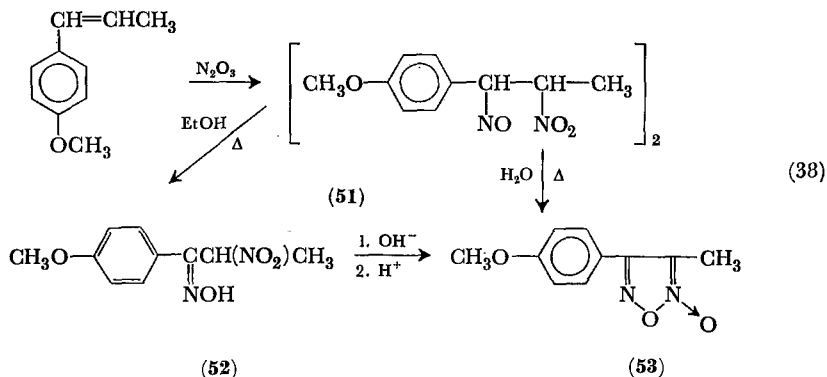
nitroso dimer **48**. The dimer is easily converted to **49** in hot alcohol, (equation 36). *p*-Anisalacetophenone reacts with dinitrogen trioxide



to give a nitroso dimer in 15% yield<sup>104</sup>. In hot alcohol, the dimer is



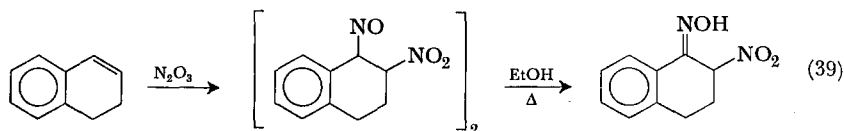
converted to the isoxazole **50** (equation 37). The addition of dinitrogen trioxide to anethole forms a nitroso dimer **51**. The nitroxime **52** is obtained by heating the dimer in alcohol, but a furoxan **53** is produced by heating the dimer in water<sup>103</sup> (equation 38). The



nitroxime **52** is readily converted to the furoxan **53**, and Wieland's research delineates the problem of converting the nitroso dimers to useful compounds.

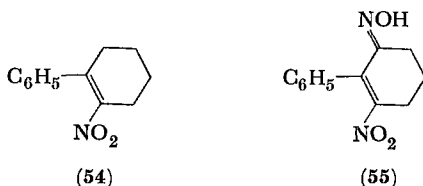
Styrene reacts with dinitrogen trioxide to form a nitroso dimer<sup>105</sup> which is converted to *o*-nitroacetophenone oxime and *o*-nitroacetophenone<sup>106</sup>. Camphene reacts with oxides of nitrogen to form *o*-nitrocamphene in 40% yield according to Lipp's procedure<sup>107</sup>. The product from 3,4-dihydronaphthalene and oxides of nitrogen

is probably a nitroso dimer. Dissociation and isomerization of the dimer to 2-nitro-1-tetralone oxime is accomplished in hot ethanol (equation 39), and the oxime is an intermediate for the preparation of heterocyclic compounds<sup>108</sup>. The addition of oxides of nitrogen to



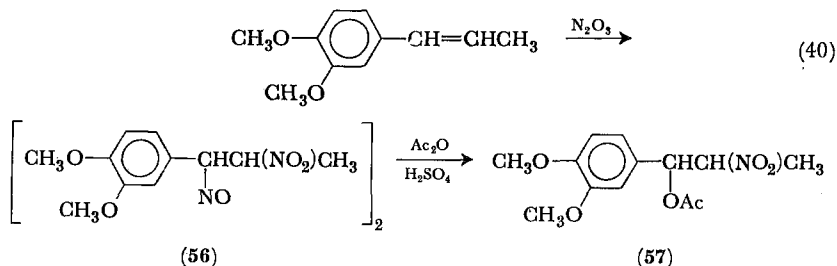
several olefins for the preparation of pseudonitrosites is described<sup>109</sup>. The pseudonitrosites are converted to nitroximes in polar solvents such as dimethyl sulfoxide and dimethylformamide. Furoxans are prepared by the dehydration of nitroximes in concentrated sulfuric acid.

Dinitrogen trioxide reacts with 1-phenylcyclohexene<sup>110</sup> to give predominantly 2-nitro-1-phenylcyclohexene (**54**) after immediate workup. When the reaction mixture is allowed to stand for several hours, the main product is 3-nitro-2-phenylcyclohexenone oxime (**55**). The reaction furnishes analogs of **54**; after reduction and



acylation, phenanthridine derivatives are available by cyclization<sup>111</sup>. Unsaturated nitro compounds are also obtained from the reaction of dinitrogen trioxide with 1-phenylcyclopentene and 1-phenylcycloheptene<sup>110</sup>.

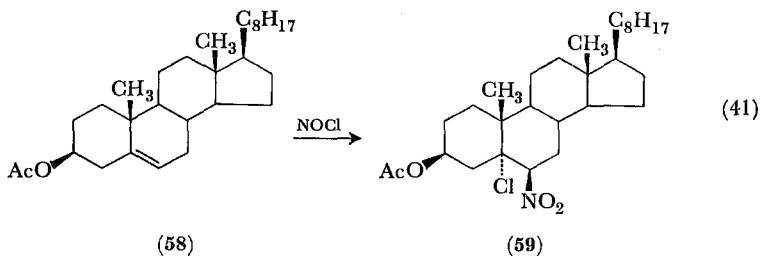
The preparation of phenanthridines is an adaptation of Bruckner's method for the synthesis of isoquinolines<sup>112</sup>. Decomposition of the nitroso dimer **56** yields **57** (equation 40). Reduction, acylation, and



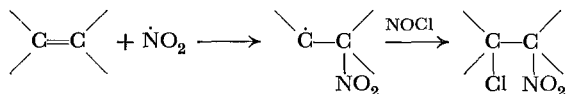
cyclization complete the synthetic sequence to an isoquinoline compound.

### E. Nitrosyl Chloride

Cholesteryl acetate (**58**) reacts with nitrosyl chloride<sup>113,114</sup> to give the 5 $\alpha$ -chloro-6 $\beta$ -nitro compound **59** in 92% yield (equation 41). This surprising result is supplemented by the observation<sup>114</sup> that the



reaction with pure nitrosyl chloride is slow. In the presence of nitrogen dioxide the nitrochloride **59** is formed rapidly, probably by a free radical mechanism. Two additional examples of the reaction



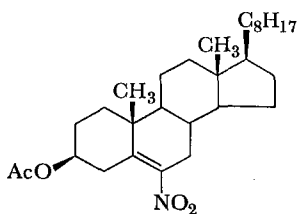
with unsaturated steroids<sup>113</sup> are given, and the yields are over 80%.

The same product, 1-chloro-2-nitro-1,1,2,2-tetrafluoroethane, is obtained from the reaction of tetrafluoroethylene with nitrosyl chloride or with nitryl chloride<sup>115</sup>.

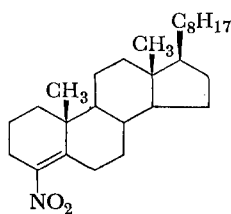
### F. Nitric Acid

The nitration of carbon-carbon double bonds with nitric acid is applicable to the synthesis of nitro steroids<sup>16,116</sup>. Nitration of cholesteryl acetate<sup>117,118</sup> is effected by fuming nitric acid, and the yield of 6-nitrocholesteryl acetate (**60**) is 79%. In a similar way  $\Delta^4$ -cholestene<sup>16,119</sup> affords the unsaturated nitro steroid **61** in 75% yield. The nitration products of  $\Delta^7$ -,  $\Delta^{9(11)}$ -, and  $\Delta^{7,9(11)}$ -unsaturated steroids are reported by Anagnostopoulos and Fieser<sup>118</sup>.

Nitration studies of steroids have been extended to the preparation of 6 $\alpha$ - and 6 $\beta$ -nitro derivatives of testosterone, progesterone, and

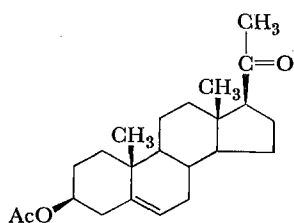


(60)

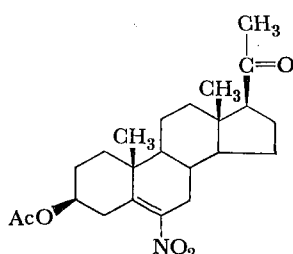


(61)

$\Delta^4$ -androstene-3,17-dione<sup>120</sup>. Nitration of pregnenolone acetate (**62**)



(62)

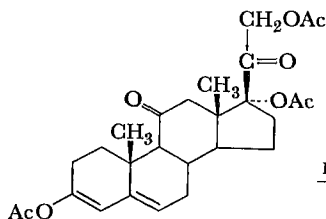


(63)

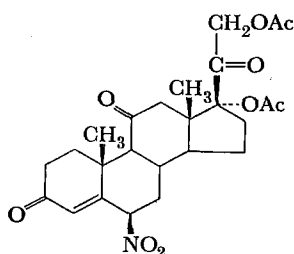
(42)

affords 6-nitropregnenolone acetate (**63**) in 62 % yield (equation 42).

The nitration of a  $\Delta^{3,5}$ -dienylacetate provides another route to nitro steroids<sup>121</sup>. On nitration, the dienylacetate **64** gives **65** in 49 %



(64)

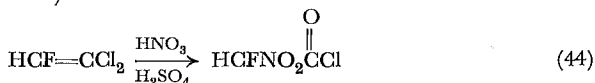


(65)

(43)

yield (equation 43). Mild alkaline treatment of **65** yields 6 $\alpha$ -nitrocortisone. Demonstrating the utility of the method, 6 $\alpha$ -nitrotestosterone is available by an analogous sequence of reactions.

Fluoronitroacetyl chloride, which can readily be converted to its derivatives, is prepared by nitration of 1,1-dichloro-2-fluoroethylene<sup>122</sup> (equation 44).

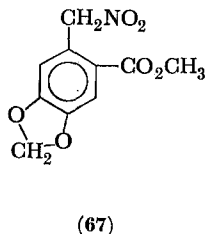
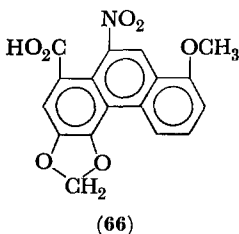


## VI. DISPLACEMENT REACTIONS BY NITRITE IONS

### A. Silver Nitrite

#### 1. General nature of the reaction

Victor Meyer and O. Stüber discovered the reaction of silver nitrite with alkyl iodides in 1872<sup>123</sup>. Nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, and nitropentane were prepared, and alkyl nitrites were recognized as secondary products of the reaction. Today the reaction of silver nitrite with an alkyl halide, the Victor Meyer reaction, is one of the established methods for the preparation of primary nitroalkanes<sup>124,125</sup>, aryl nitromethanes<sup>126</sup>, and  $\alpha$ -nitro esters<sup>127</sup>. The reaction is useful for the preparation of  $\alpha,\omega$ -dinitroalkanes<sup>128</sup>, but the reaction is not suitable for the preparation of secondary and tertiary nitroalkanes. The synthesis<sup>129</sup> of aristolochic acid (**66**), a naturally occurring nitro compound which is the tumor-inhibitory principle of *Aristolochia indica* L., includes the preparation of **67**; an appropriate recent application of the Victor Meyer reaction.



#### 2. Stereochemistry and mechanism

The reaction of silver nitrite in diethyl ether with optically active 2-bromooctane occurs to give 2-nitrooctane and 2-octyl nitrite with inversion of configuration<sup>130</sup>. The role of the nitrite ion as a nucleophile is important, and failure of neopentyl iodide to react under conditions which facilitate complete reaction with other primary iodides must be attributed to steric conditions which prohibit nitrite ion from participating in the reaction<sup>126</sup>. These features are characteristic of a  $S_N2$  process.

The reaction of silver nitrite with alkyl halides also exhibits features which are  $S_N1$  in character, and this well-known sequence of reactivity of alkyl halides, tertiary > secondary > primary, is

typical<sup>126</sup>. The study of a series of benzyl bromides with a *para* substituent results in widely differing rates, and the reactivity sequence is that which would be expected from a carbonium ion process<sup>126</sup>. The difference in the proportion of nitro compound and nitrite ester isolated is additional evidence for the carbonium ion character of the reaction (Table 5).

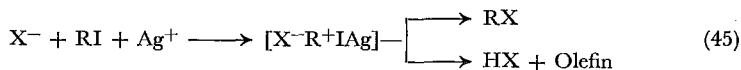
The mechanism for the reaction of alkyl halides with silver nitrite is one in which the transition state has both  $S_N1$  and  $S_N2$  character, the extent of which is dependent on the structure of the halide. Products of the reaction reflect the variation in nature of the transition state. Nucleophilic attack by nitrite ion on carbon, and electrophilic attack by the silver cation on the halogen of the alkyl halide

TABLE 5. Reaction of silver nitrite with benzyl bromides<sup>126</sup>.

Bromide	Half-life minutes	Nitro compound yield, %	Nitrite ester yield, %
<i>p</i> -Nitrobenzyl	180	75	5
Benzyl	16	61	28
<i>p</i> -Methylbenzyl	1	45	37
<i>p</i> -Methoxybenzyl	very small	26	55

are essential features of the process. Formation of the silver-halogen bond provides the driving force for the Victor Meyer reaction; sulfonate esters fail to react with silver nitrite<sup>126</sup>.

There is agreement that the mechanism for the reaction of silver salts with alkyl halides must inscribe both  $S_N1$  and  $S_N2$  properties<sup>131</sup>. An excess of nitrate ion accelerates the reaction of silver nitrate with ethyl iodide, but the yield of products, ethyl nitrate and nitric acid, is independent of the concentration of nitrate ion<sup>132,133</sup>. This requires that the rate-determining step and product-determining step be different. An ion-pair mechanism accommodates these observations<sup>132</sup> (equation 45).



### 3. Synthesis

The reaction of silver nitrite with primary alkyl iodides or bromides is an excellent method for the preparation of primary nitroalkanes<sup>124,125,134</sup> with the exception of neopentyl iodide<sup>126</sup>. The

reaction fails with primary alkyl chlorides. The difference in reactivity of alkyl halides with silver nitrite is of interest, and several  $\alpha$ -fluoro- $\omega$ -bromoalkanes are converted to  $\alpha$ -fluoro- $\omega$ -nitroalkanes<sup>135</sup>. The success of the Victor Meyer reaction is closely related to the structure of the halide, and it is apparent from the data in Table 6 that secondary alkyl iodides or bromides are not suitable for the preparation of secondary nitroalkanes<sup>136</sup>. Branching of the carbon

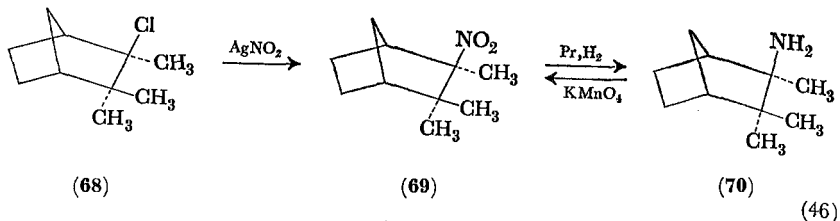
TABLE 6. Synthesis of nitro compounds by the Victor Meyer reaction.

Nitro compound	Yield %	RX X	Reference
$n\text{-C}_4\text{H}_9\text{NO}_2$	73	Br	125
$n\text{-C}_5\text{H}_{11}\text{NO}_2$	67	Br	124
$n\text{-C}_8\text{H}_{17}\text{NO}_2$	80	Br	134
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{NO}_2$	72	Br	125
$(\text{CH}_3)_2\text{CHCH}_2\text{NO}_2$	59	I	125
$(\text{CH}_3)_2\text{CHNO}_2$	19-26	Br	136
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NO}_2$	19-24	Br	136
$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CHNO}_2$	7-15	Br	136
$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CH}_3)\text{NO}_2$	17-23	Br	136
$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{NO}_2$	18	Br	136
$\text{O}_2\text{N}(\text{CH}_2)_{10}\text{NO}_2$	50	I	128
$\text{F}(\text{CH}_2)_5\text{NO}_2$	73	Br	135
$\text{CH}_3\text{CH}(\text{NO}_2)\text{CO}_2\text{C}_2\text{H}_5$	80	I	127

chain is accompanied by a striking decrease in the yield of the nitro compound. With secondary bromides or iodides the products are mainly nitrite esters and olefins, and the small amounts of nitro compounds that are produced are contaminated with nitrate esters which are removable only by a chemical separation attended by loss of product.

The reaction of tertiary halides with silver nitrite for the preparation of nitro compounds is worthless<sup>136</sup>. Instead of nitro compounds, alkyl nitrites, olefins, and adducts of olefins with oxides of nitrogen are produced. Reaction of camphene hydrochloride (**68**) with silver nitrite<sup>137</sup>, and reduction of the mixture, in which the presence of the nitro compound **69** is assumed, affords **70** in low yield (equation 46). The reaction of bornylamine hydrochloride in acetic acid with sodium nitrite furnishes **69**, which is isolated and reduced to **70**. Oxidation<sup>138</sup> of the amine **70** with potassium permanganate yields the nitro

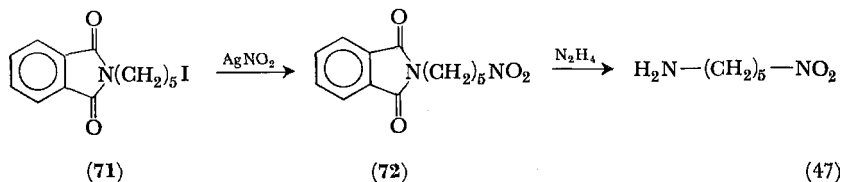




compound **69**. Though not of preparative value, the synthesis of **69** by two routes, both requiring a carbonium ion intermediate, is novel.

$\alpha$ -Nitro esters are obtained only from the corresponding  $\alpha$ -iodoesters with silver nitrite. The reaction is slow, but the yields are satisfactory<sup>127</sup>. Arylnitromethanes are available by the Victor Meyer reaction (Table 5). The reaction of silver nitrite with  $\alpha,\omega$ -diiodoalkanes forms  $\alpha,\omega$ -dinitroalkanes in 37–50% yields<sup>128</sup>.

Preparation of 1-amino-5-nitropentane involves the treatment of **71** with silver nitrite at elevated temperatures<sup>139</sup>. Cleavage of **72**



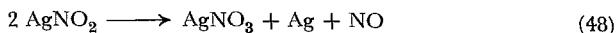
with hydrazine furnishes 1-amino-5-nitropentane (equation 47). The reaction of 1-benzoylamino-5-iodopentane with silver nitrite in a similar way provides 1-benzoylamino-5-nitropentane in 73% yield<sup>140</sup>. Blocking the reactive functional group enhances the scope of the Victor Meyer reaction.

The reaction of allyl bromide with silver nitrite leads to the corresponding nitro compound in 55% yield<sup>15</sup>. Epiiodohydrin and silver nitrite yield 1-nitro-2,3-epoxypropane. Similarly, 1-nitro-2,3-epoxybutane and 3-nitro-1,2-epoxybutane are prepared in 70 and 72% yield, respectively<sup>141</sup>.

#### 4. Experimental conditions

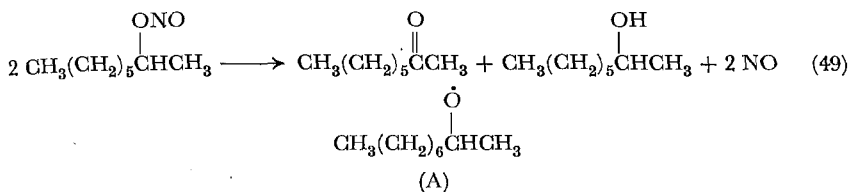
The optimum temperature range for the Victor Meyer reaction is  $0^\circ$  to room temperature. Elevated temperatures must be avoided, and the reactions of silver nitrite with 2-bromooctane<sup>142</sup> and 2-iodobutane<sup>143</sup> are illustrative. These reactions were completed on the water bath, presumably near the boiling point of benzene.

Kornblum and coworkers precisely defined the complex mixture of products from these reactions<sup>144,145</sup>. Silver nitrite decomposes above 80°, and silver nitrate is formed (equation 48). Silver nitrate reacts



with an alkyl halide to form an alkyl nitrate which is not separable from the nitroalkane by fractional distillation.

Alkyl nitrites, by-products of the Victor Meyer reaction, are thermally unstable<sup>146</sup>. For instance, the thermal decomposition of optically active 2-octyl nitrite<sup>147</sup> at 100° yields 2-octanone and optically pure 2-octanol (equation 49). The intermediate free



radical (A) does not racemize.

At elevated temperatures the products of the reaction of silver nitrite with 2-bromooctane are mainly 2-nitrooctane and 2-octyl nitrite; by-products are 2-octyl nitrate, 2-octanone, and 2-octanol<sup>144</sup>. Similarly, the reaction of silver nitrite with 2-iodobutane forms 2-nitrobutane, 2-butyl nitrite, 2-butyl nitrate, 2-butanol, and butanone<sup>145</sup>.

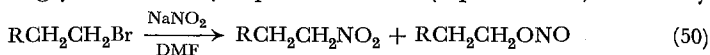
Silver nitrite<sup>134</sup> is suspended in anhydrous diethyl ether, the most suitable medium; although benzene, hexane and petroleum ether are satisfactory. Silver nitrite is soluble in acetonitrile, but undesirable side-reactions may destroy the product<sup>148</sup>. The instability of silver salts and alkyl nitrites to light requires that the reaction be protected from light until the separation of products has been completed. Experimental procedures published since Kornblum's work in 1947 are the best procedures for the Victor Meyer reaction (Tables 5 and 6).

## B. Alkali Metal Nitrites

### 1. General nature of the reaction

Use of the alkali metal nitrites in place of silver nitrite for the preparation of nitroalkanes requires that both nitrite and halide be in solution<sup>149,150</sup>. Although lithium nitrite is more soluble than

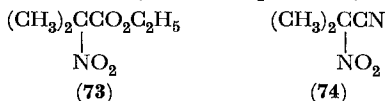
sodium nitrite in the solvents that are used, sodium nitrite is employed because of its availability. Dimethylformamide is the optimum solvent; dimethyl sulfoxide is useful with certain limitations, and ethylene glycol is clearly a poorer choice (equation 50). Primary



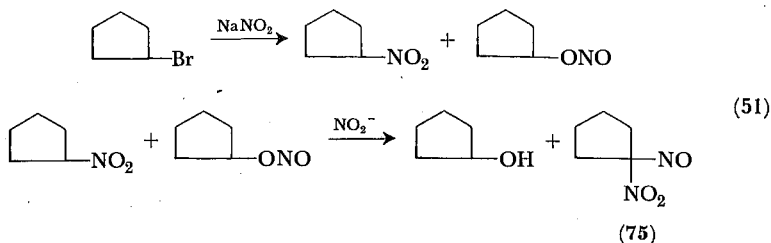
and secondary alkyl iodides and bromides, as well as sulfonate esters, are satisfactory for the preparation of primary and secondary nitroalkanes. The reaction of alkyl chlorides with sodium nitrite is too slow to be useful. Use of *t*-butyl halides with sodium nitrite for the preparation of nitro compounds is worthless. The modified Victor Meyer reaction is applicable to the synthesis of  $\alpha$ -nitro esters<sup>151,152</sup> and  $\beta$ -nitroketones<sup>153</sup>. Failure of cyclohexyl bromide to react with sodium nitrite to form nitrocyclohexane is a serious limitation<sup>150</sup> which precludes the application of the modified Victor Meyer reaction to the synthesis of nitro steroids<sup>16</sup>.

## 2. Mechanism

In dimethylformamide the reaction of sodium nitrite with primary or secondary alkyl bromides forms the nitroalkanes in yields of 55–60%; the nitrite esters are formed in yields of 30–33%. The reaction of an alkyl bromide with nitrite ion is, not unexpectedly, a  $\text{S}_{\text{N}}2$  reaction<sup>148,149,126</sup>. The application of the modified Victor Meyer reaction should succeed where  $\text{S}_{\text{N}}2$  reactions may be operative. Failure of *trans*-1,4-cyclohexanediol *bis-p*-toluenesulfonate to react with sodium nitrite in dimethylformamide is attributed to the presence of large leaving groups in the equatorial position and consequent crowding by axial hydrogens which hinder attack by the nitrite ion<sup>154</sup>. A reaction does occur between cyclohexyl iodide and sodium nitrite; cyclohexene is isolated in 57% yield<sup>150</sup>. Ethyl  $\alpha$ -bromoisobutyrate<sup>151</sup> and  $\alpha$ -bromoisobutyronitrile<sup>148</sup> react to form **73** and **74** in 78% and 50% yields, respectively.

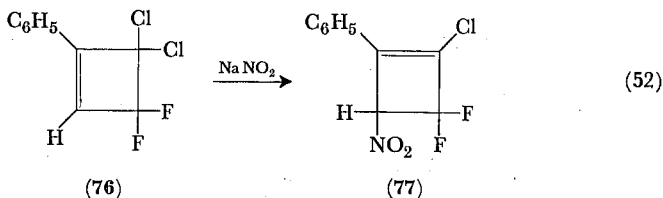


The rate of reaction of *n*-butyl bromide with sodium nitrite is one thousand times faster in dimethylformamide than in ethylene glycol<sup>148</sup>. Destruction of the nitroalkane under conditions of the reaction emphasizes the importance of a rapid reaction for the synthesis to be useful. Nitrocyclopentane is converted to the pseudo-nitrole **75** in the presence of nitrite ester and nitrite ion<sup>155</sup> (equation

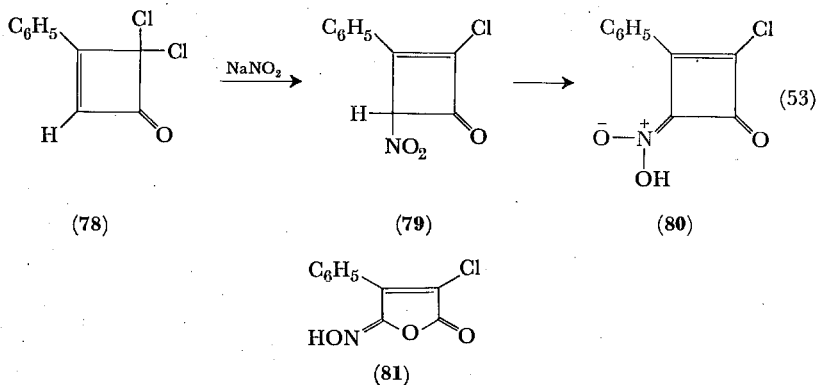


51), and  $\alpha$ -nitro esters under similar conditions are degraded to  $\alpha$ -oximinooesters<sup>151</sup>.

The nitrocyclobutene **77** is prepared in 54% yield by the reaction of 1-phenyl-3,3-difluoro-4,4-dichlorocyclobutene (**76**) with sodium nitrite<sup>156</sup> (equation 52). Cyclobutenyl halides undergo  $S_N2'$  displacement reactions<sup>157</sup>, and Breslow and coworkers report the first



example of the nitrite ion reacting in a  $S_N2'$  process. Another interesting example is the reaction of 2,2-dichloro-3-phenylcyclobutenone (**78**) with sodium nitrite to give the nitrocyclobutenone **79**. The infrared spectrum shows a hydroxyl band at  $2.83 \mu$ , carbonyl absorption at  $5.60 \mu$ , and no bands characteristic of a nitro group. The nmr spectrum shows five phenyl protons at  $\delta$  7.7 and one proton at  $\delta$  11.1. These spectra require that the *aci*-nitro structure **80** be assigned to the product<sup>156</sup> (equation 53). There is a



possibility that a rearrangement may have occurred, and **81** also conforms to the physical data<sup>156</sup>.

### 3. Synthesis

Higher yields of primary nitro compounds are obtained by the reaction of silver nitrite with primary alkyl bromides or iodides than by the use of sodium nitrite. However, the yields are adequate with sodium nitrite (Table 7) and the availability and convenience of

TABLE 7. Synthesis of nitro compounds with sodium nitrite.

Nitro compound	Yield %	RX X	Reference
1-Nitroheptane	60	Br	150
1-Nitrooctane	60	I	150
1-Nitrooctane	45	tosylate	149
1-Nitro-3-phenylpropane	58	I	150
Nitrocyclopentane	57	Br	150
Nitrocyclohexane	0	I	150
Nitrocycloheptane	58	I	150
Ethyl $\alpha$ -nitrocaproate	74	Br	151
Ethyl $\alpha$ -phenyl- $\alpha$ -nitroacetate	70	Br	152
2-Nitrooctane	58	Br	150
4-Nitroheptane	61	Br	150
Phenylnitromethane	55	Br	150
1,4-Dinitrobutane	33	Br	164
1,6-Dinitrohexane	42	Br	164
4-Nitro-2-butanone	47	Cl	153
1-Nitro-3-pentanone	48	Cl	153
2-Nitropropiophenone	87	Br	153

sodium nitrite make the two methods equally satisfactory. The yields of secondary nitroalkanes by the reaction of sodium nitrite with secondary alkyl bromides are substantially higher than those from the reaction with silver nitrite. In the preparation of  $\alpha$ -nitro esters sodium nitrite is again superior to silver nitrite which requires the unavailable  $\alpha$ -iodesters, whereas sodium nitrite reacts with  $\alpha$ -chloro and  $\alpha$ -bromoesters.

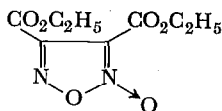
4-Bromo-1-butene reacts with sodium nitrite in dimethyl sulfoxide to yield 4-nitrobut-1-ene, an intermediate necessary for the synthesis of sinigrin<sup>158</sup>. Thus, unsaturated alkyl bromides react to form nitro compounds, but there is scant information about the reaction of allyl halides with sodium nitrite. Sodium nitrite does not react with

6 $\beta$ -bromotestosterone to form a nitro steroid<sup>120</sup>; the product of the reaction, if any, is not reported.

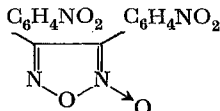
Sodium nitrite reacts with  $\beta$ -propiolactone<sup>159</sup> to form sodium 3-nitropropionate; the nitro acid is isolated in 47% yield. The 3-nitropropionic acid, one of the few naturally occurring nitro compounds, is the toxic principle<sup>160</sup> of *Indigofera endicaphylla* Jacq. Methyl  $\gamma$ -nitrovalerate is hydrolyzed to  $\gamma$ -nitrovaleric acid by concentrated hydrochloric acid in 92% yield<sup>161</sup>.

The reaction of ethylene oxide with aqueous barium nitrite is not useful for the preparation of 2-nitroethanol<sup>162, 163</sup>. Cyclohexene oxide reacts with diisopropylammonium nitrite to furnish *trans*-2-nitrocyclohexanol in 23% yield<sup>163</sup>. The conversion of 1-iodo-2,3-epoxybutane to 1-nitro-2,3-epoxybutane in 70% yield<sup>141</sup> indicates that the oxide ring is, for the most part, resistant to attack by nitrite ion. In aprotic solvents in which the reactions of alkali nitrites must be done, the first intermediate from a reaction with an oxide could reasonably be expected to eliminate nitrite ion and revert to reactant.

The reaction of  $\alpha, \omega$ -dibromoalkanes with sodium nitrite provides  $\alpha, \omega$ -dinitroalkanes<sup>164</sup> in low yields (29–42%), and the preparation of  $\alpha, \omega$ -dinitroalkanes by this method is inferior to the preparation by the Victor Meyer reaction<sup>165</sup>. In addition to the limitations which have already been discussed, the modified Victor Meyer reaction has several other deficiencies. Ethyl bromoacetate reacts with sodium nitrite to form the furoxan **82** in 48% yield<sup>166</sup>; usually the reaction of homologs is successful for the synthesis  $\alpha$ -nitro esters<sup>151</sup>. The reaction of 21-iodoprogesterone with sodium nitrite does not form 21-nitroprogesterone<sup>167</sup>, and the product of this reaction is not reported. There is little information available on the reaction of  $\alpha$ -haloketones with sodium nitrite. The reaction of *p*-nitrobenzyl bromide with sodium nitrite<sup>166</sup> forms *p*-nitrophenylnitromethane in 22% yield and the furoxan **83** in 31% yield. At the same time the *p*-nitrobenzyl nitrite<sup>166</sup> that is formed undergoes degradation with surprising ease to *p*-nitrobenzaldehyde (24% yield) and the acetal (72% yield) of *p*-nitrobenzaldehyde with *p*-nitrobenzyl alcohol. Presumably, similar difficulties were encountered by Muth and coworkers<sup>168</sup>. The reaction is satisfactory with benzyl bromide itself,



(82)



(83)

and phenylnitromethane is obtained in 55% yield. Functional groups that increase the acidity of the desired nitro compound in comparison to a nitroalkane or arylnitroalkane, facilitate a nitrosation reaction which destroys the product<sup>166</sup>. When long periods of reaction are necessary or when the product is susceptible to nitrosation, phloroglucinol is added to scavenge the nitrite ester.

The reaction of sodium chloroacetate with sodium nitrite furnishes nitromethane<sup>169</sup> in 38% yield, but the reaction is not suitable for the preparation of homologs<sup>150</sup>.

#### 4. Experimental conditions

Dimethyl sulfoxide and *N,N*-dimethylformamide dissolve appreciable quantities of the alkali metal nitrites and are the optimum solvents for the modified Victor Meyer reaction. Some halides react with dimethyl sulfoxide<sup>170</sup> (equation 54) and the references in

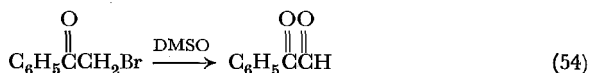


Table 7 will be useful in selection of the proper solvent. The solubility of sodium nitrite is increased substantially by the addition of urea, but the addition of urea does not increase the solubility of potassium nitrite comparably. Lithium nitrite is the most soluble in dimethylformamide, but is not commercially available. Treatment of lithium carbonate with perchloric acid yields lithium perchlorate, and addition of potassium nitrite results in the precipitation of potassium perchlorate. After removal of the precipitate, lithium nitrite is isolated from the filtrate<sup>148</sup>.

The reaction of sodium nitrite with alkyl halides is slightly exothermic, and the reaction is usually maintained at room temperature. Lower temperatures ( $-15^\circ$  to  $-20^\circ$ ) are necessary in the preparation of phenylnitromethane. It is important that the products of the modified Victor Meyer reaction be isolated promptly when the reaction is over. The amount of time for the reaction is dependent on the structure of the halide, and these details are to be found in the references given in Table 7.

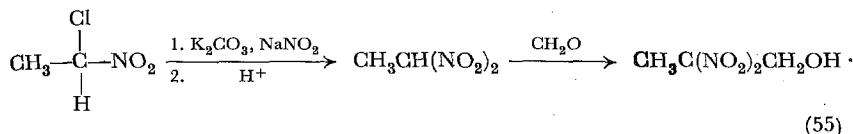
### VII. POLYNITRO COMPOUNDS

Several methods of preparing polynitro compounds are described in other sections of this chapter, and a preparation of *gem*-dinitro

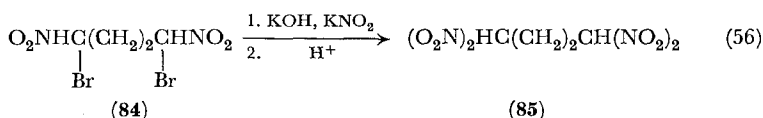
compounds is presented in section II.A. Formation of a dinitro compound by oxidation of a diamine is reported in section III.B. Synthesis of  $\alpha,\omega$ -dinitro compounds by the alkyl nitrate nitration process are described in section IV.A. The conversion of olefins to 1,2-dinitro compounds is related in section V.C. The preparation of  $\alpha,\omega$ -dinitroalkanes by the Victor Meyer reaction (section VI.A.) and by the modified Victor Meyer reaction (section VI.B.) from  $\alpha,\omega$ -dibromoalkanes has also been described. The synthesis of aliphatic polynitro compounds is the subject of a recent review<sup>171</sup>.

### A. ter Meer Reactions

In 1876, ter Meer published a convenient method for the synthesis of *gem*-dinitro compounds. He described the reaction of sodium nitrite with 1-bromo-1-nitropropane, which provided 1,1-dinitropropane, and he also prepared 1,1-dinitroethane<sup>172</sup>. Earlier, Meyer and Raillet had observed that the sodium salt of nitroethane brominated readily<sup>123</sup>. Chlorination<sup>173</sup> of nitroethane in aqueous sodium hydroxide affords 1-chloro-1-nitroethane in a conversion of 95%. The ter Meer reaction with 1-chloro-1-nitroethane followed by an



aldol condensation with formaldehyde at a pH of seven produces 2,2-dinitropropanol in an overall yield of 60% from nitroethane<sup>174</sup> (equation 55). Synthesis of  $\alpha,\alpha,\omega,\omega$ -tetranitroalkanes is another useful application of the ter Meer reaction<sup>175</sup>. The disodium salt of 1,4-dinitrobutane is brominated quantitatively to **84**, consisting of a

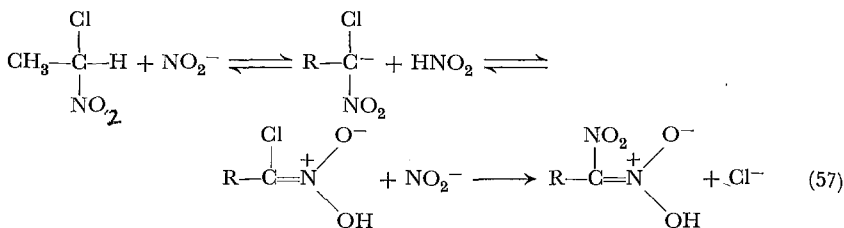


mixture of diastereoisomers. Subsequent reaction with potassium hydroxide and potassium nitrite furnishes **85** after acidification in a yield of 28% (equation 56).

The mechanism of the ter Meer reaction has been established by Hawthorne<sup>176</sup>. Reaction of 1-chloro-1-nitroethane with nitrite ion occurs through the isomerization of the chloronitroethane to its *aci*-nitro isomer, and a nucleophilic displacement of chloride by



nitrite ion completes the reaction (equation 57). The reaction is inhibited by excess strong base; therefore the nitronic acid must be

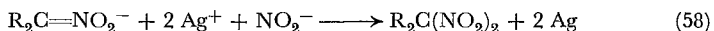


present. At high nitrite ion concentrations, the reaction shows a first-order dependence on both nitrite ion and chloronitroethane. The rate-determining process is the ionization of chloronitroethane catalyzed by nitrite ion. When 1-chloro-1-nitroethane-1-d is used, a primary kinetic isotope effect of 3.3 is obtained.

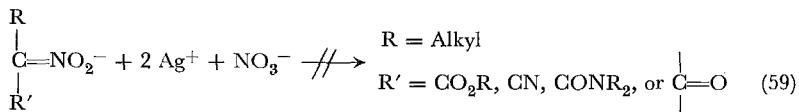
## B. Kaplan-Shechter Reaction

### 1. General nature of the reaction

Preparation of *gem*-dinitro compounds by the reaction of salts of primary or secondary nitro compounds with silver nitrate and inorganic nitrites in alkaline or neutral media is a recent discovery by R. B. Kaplan and H. Shechter<sup>177</sup> (equation 58). The oxidative



nitration reaction is an excellent method for the synthesis of *gem*-dinitroalkanes, and the new reaction is successful for hindered compounds. The reaction is not effective with nitro compounds which have an electron withdrawing group *alpha* to the carbon bearing the nitro group<sup>165</sup> (equation 59). A comparison of the ter

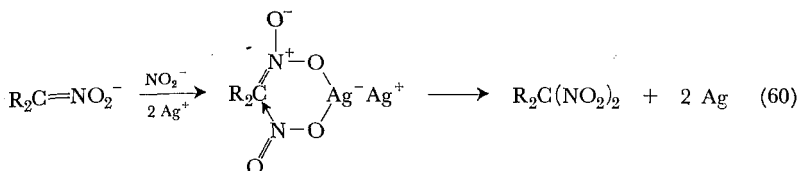


Meer reaction and the Kaplan-Shechter reaction has been published<sup>174</sup>.

### 2. Mechanism

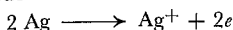
Kaplan and Shechter propose that the reaction occurs by formation of a complex salt, the steric nature of which favors decomposition

to the dinitro compound (equation 60).

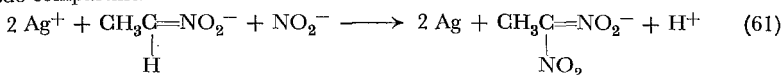


The Kaplan-Shechter reaction has been modified to an electrolytic process<sup>178</sup>. The following reactions occur in the electrolytic cell (equation 61). Wright and Levering<sup>178</sup> propose that an intermediate

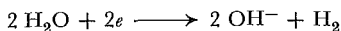
Anode



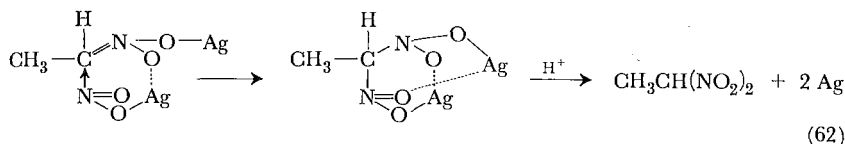
Anode compartment



Cathode



complex, which contains nitrite, ethyl nitronate, and silver ions in a mole ratio of 1:1:2, is formed (equation 62).



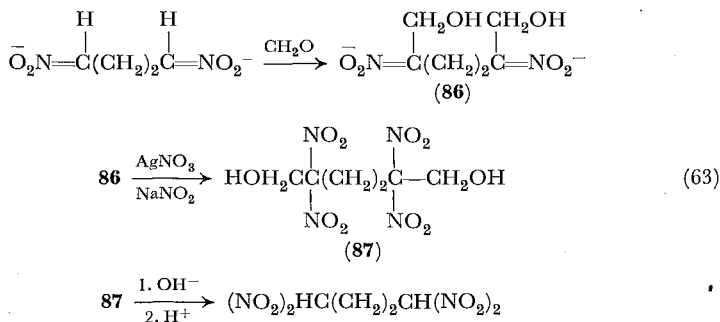
Association of the nitrite ion with silver, which is already associated with nitroethane, is essential to account for the specificity of C—N bond formation. The silver ions are probably coordinated with water or hydroxyl ions in a four coordinated tetrahedral structure, and decomposition of the complex by hydrogen ions permits the formation of an intermetallic bond between two favorably located silver atoms with a resultant redistribution of the electrons. According to these concepts the driving force for the reaction is the formation of the silver dimer.

The mechanism of the Kaplan-Shechter reaction has not been studied intensively. Both of the suggested mechanisms invoke the internal delivery of nitrite ion via a complex salt to explain the exclusive formation of the C—N bond. Silver nitrate and mercuric nitrate are the only effective oxidizing agents for the preparation of *gem*-dinitro compounds<sup>177</sup> by this method.

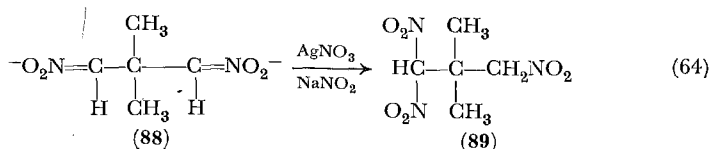
### 3. Synthesis

Yields in the oxidative nitration reaction vary from 60 to 95%. The preparation of primary, secondary, and functionally-substituted dinitro compounds are reported<sup>177</sup>. Typical examples are the synthesis of 1,1-dinitropropane, 2,2-dinitrobutane, 1,1-dinitrocyclohexane, 2,3-dimethyl-2,4,4-trinitropentane, methyl 3,3-dinitropropionate, and 1-cyclopropyl-1,1-dinitroethane. The reaction of phenylnitromethane with silver nitrate and sodium nitrite, in alkaline solution yields four products: phenyldinitromethane (19%), *meso*-1,2-dinitro-1,2-diphenylethane (12%), *d,l*-1,2-dinitro-1,2-diphenylethane (25%), and benzaldehyde (36%). The oxidation of 2-nitro-1,3-propanediol forms 2,2-dinitro-1,3-propanediol (70–80% yield), which undergoes a reverse aldol reaction in alkaline solution to furnish dinitromethane.

The direct Kaplan-Shechter reaction fails on  $\alpha,\omega$ -dinitro compounds in which the nitro groups are not separated by at least four methylene groups<sup>165</sup>, but with 1,6-dinitrohexane and 1,7-dinitroheptane the yields of tetranitro products are 84 and 89%, respectively. The technique of converting primary nitro compounds to secondary nitro derivatives broadens the scope of the new reaction<sup>179</sup>. The aldol condensation of 1,4-dinitrobutane with formaldehyde yields the aldol **86**, which is not isolated. Addition of silver nitrate and sodium nitrite to **86** produces **87**. The reverse aldol reaction is effected in alkaline media, and after acidification, 1,1,4,4-tetranitrobutane is isolated in an overall yield of 49% (equation 63).



In some instances the Kaplan-Shechter reaction takes an abnormal course<sup>177</sup>. Only partial nitration may occur. Thus oxidative nitration of **88** furnishes **89**, a trinitro compound, instead of the expected tetranitro product (equation 64). Oxidative nitration of



salts of 1,1-dinitro compounds to the corresponding 1,1,1-trinitro derivatives does not occur.

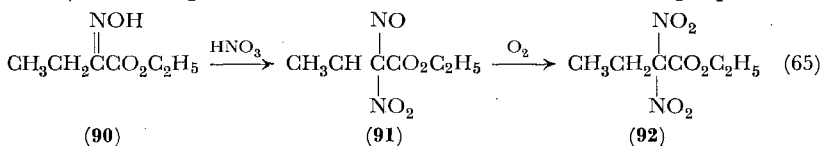
#### 4. Experimental conditions

The experimental procedures appear to be quite simple in the original publication<sup>177</sup>.

The oxidative dimerization of secondary nitroalkanes is also described by Kaplan and Shechter<sup>180</sup>. For example, the oxidation of sodium 2-propanenitronate with sodium persulfate at a pH of 9.4–7.2 produces 2,3-dimethyl-2,3-dinitrobutane in 53% yield. Persulfates are the most effective agents for the dimerization and 1,1'-dinitrobicyclohexyl is obtained in 30% yield from nitrocyclohexane and ammonium persulfate in alkaline solution.

#### C. Oxidation of Pseudonitroles

The oxidation of pseudonitroles is a well-known reaction which can be effected by a large number of oxidants. Chromium trioxide in acetic acid, nitric acid, hydrogen peroxide, peroxytrifluoroacetic acid, or oxygen are oxidizing agents that have been employed. As an illustration, ethyl  $\alpha$ -oximinobutyrate (**90**) is added to a cold solution of 100% nitric acid containing ammonium nitrate. The pseudonitrole **91** is obtained in 93% yield. Air oxidation of the pseudonitrole forms the  $\alpha,\alpha$ -dinitro ester **92** in 64% yield<sup>181</sup> (equation 65). The sequence of reactions is successful for the preparation

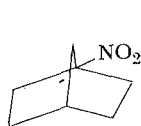


of  $\alpha,\alpha$ -dinitro esters. However, Noland and Libers<sup>182</sup> report the oxidation of pseudonitroles to *gem*-dinitro compounds in low yields that vary from 5–20%.

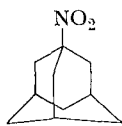
#### D. Other Methods

Polynitro compounds may form by internal displacement reactions. The nitrate ester **93** is among the products formed by the reaction of





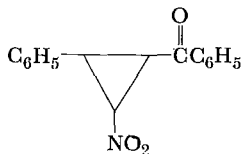
(100)



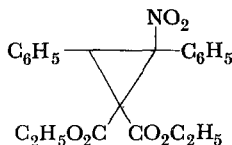
(101)

150–200° in carbon tetrachloride with nitrogen dioxide yields mainly 2-nitrobicyclo[2.2.1]heptane<sup>188</sup>. The syntheses of **100** and **101** appear to be the only examples of nitration at the bridgehead position<sup>189</sup>. Synthesis of a bridgehead nitro compound by an internal alkylation reaction<sup>29</sup> is described in section II.B, and the rearrangement of 2-bromo-2-nitrobornane to 1-nitrocamphene provides a route to several bridgehead nitro derivatives<sup>190</sup>. Bridgehead nitro compounds are of interest for conversion to amines, following the discovery of the viruscidal properties of 1-aminoadamantane.

Nitration of cyclopropane in the vapor phase with nitric acid at temperatures of 390–410° and with dinitrogen tetroxide at atmospheric pressure in the gas phase at 420–455° furnishes nitrocyclopropane<sup>191</sup>. Unlike secondary nitroalkanes, nitrocyclopropane does not dissolve in strong aqueous bases, and it does not form salts in homogeneous alkaline media at 25°. Nitrocyclopropane derivatives have been prepared by several methods. Diphenyldiazomethane adds to nitroethylene to give 1-nitro-2,2-diphenylcyclopropane.<sup>192</sup> Cyclization reactions applicable to the synthesis of a cyclopropane ring<sup>193,194</sup> yield 2-nitrocyclopropyl ketone (**102**) and the nitro compound **103**.



(102)

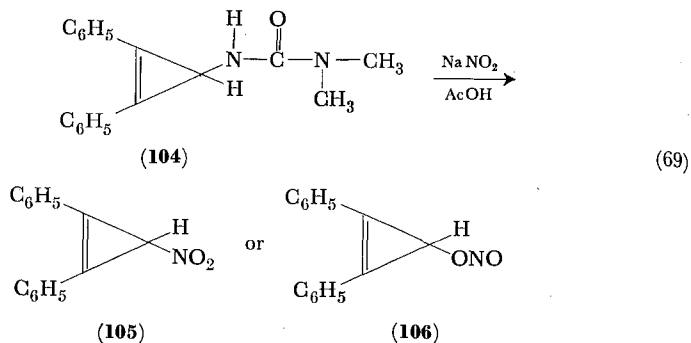


(103)

Nitration of optically active 3-methylheptane with nitrogen dioxide in the liquid phase yields racemic 3-methyl-3-nitroheptane<sup>189</sup>. Nitrogen dioxide abstracts a hydrogen atom from 3-methylheptane to form the 3-methyl-3-heptyl radical which is then converted to racemic 3-methyl-3-nitroheptane. Nitration of *cis*- and *trans*-decalins with nitric acid in the liquid phase yields *trans*-9-nitrodecalin as the main tertiary nitration product<sup>189</sup>. Nitration of *cis*- and *trans*-hydrindanes yields the same 8-nitrohydrindane<sup>189</sup>. Thus, nitration

occurs preferentially, but not exclusively, at tertiary carbon atoms. It is worthy of note that these nitrations occur without skeletal rearrangement.

Reaction of **104** in acetic acid and acetic anhydride with sodium nitrite affords 1,2-diphenyl-3-nitrocyclopropene (**105**) or 2,3-diphenyl-2-cyclopropenyl nitrite (**106**) in 67 % yield<sup>195</sup> (equation 69).



The infrared spectrum suggests the nitrocyclopropene structure, and the nmr spectrum also supports the same structure. The ultraviolet spectrum is characteristic of a 1,2-diphenylcyclopropene. That the compound is not a dimer is revealed by its mass spectrum. Chemical reactions of the product are difficult to interpret because of the ease with which the cyclopropenyl cation may be expected to form. The method of synthesis favors the nitrite **106**, although another carbonium ion under similar circumstances gave a nitro compound in low yield<sup>137</sup>. 1,2-Diphenylcyclopropenyl perchlorate on treatment with sodium nitrite in acetic acid and acetic anhydride gave a quantitative yield of **105** or **106**. The evidence is not sufficiently conclusive to distinguish between the two structures at the present time. Thus, the structure does not necessarily follow from synthesis, and the product may be a nitro compound with novel properties.

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## CHAPTER 7

# Nitronic acids and esters

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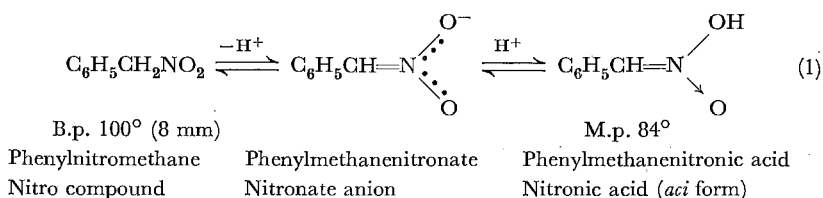
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I. INTRODUCTION . . . . .	350
II. <i>ACI</i> -NITRO TAUTOMERISM . . . . .	352
A. Introduction . . . . .	352
B. Tautomerization of Nitronic Acids to Nitroalkanes . . . . .	353
C. Proton Removal from Nitroalkanes . . . . .	364
D. Ionization Constants of Nitronic Acids and Nitroalkanes . . . . .	372
III. NITRONIC ACIDS . . . . .	376
A. Preparation of Nitronic Acids . . . . .	376
B. Physical Properties of Nitronic Acids . . . . .	382
C. Reactions of Nitronic Acids . . . . .	384
1. Addition reactions of nitronic acids . . . . .	384
a. Nucleophilic addition . . . . .	384
b. Electrophilic addition . . . . .	393
2. Oxidation and reduction reactions . . . . .	398
3. Reactions of $\alpha$ -halonitronic acids . . . . .	404
4. Reactions of ketonitronic acids . . . . .	406
IV. NITRONIC ACID ESTERS . . . . .	417
A. Preparation of Nitronic Acid Esters . . . . .	417
1. Acyclic nitronic acid esters . . . . .	417
2. Cyclic nitronic acid esters . . . . .	430
B. Physical Properties of Nitronic Acid Esters . . . . .	435
C. Reactions of Nitronic Acid Esters . . . . .	437
1. Hydrolysis of nitronic esters . . . . .	437
2. Oxidation and reduction reactions of nitronic acid esters . . . . .	443
3. 1,3-Dipolar addition reactions of nitronic acid esters . . . . .	453
V. NITRONIC ACID DERIVATIVES OTHER THAN ESTERS . . . . .	459
A. Nitronic Acid Salts . . . . .	459
B. Nitronic Acid Anhydrides . . . . .	461
C. Nitronic Acid Halides . . . . .	468
D. Nitronic Acid Amides . . . . .	469

VI. ANALYTICAL METHODS FOR NITRONIC ACIDS	470
VII. REFERENCES	473

## I. INTRODUCTION

The nitronic acids, or *aci*-nitro compounds,  $R^1R^2C=NO_2H$ , are an important group of organic acids. They may be characterized as rather unstable substances and good oxidizing agents, as are their esters. Most are relatively weak acids ( $pK_a^{aci}$  2-6) resembling carboxylic acids in acid strength. They are somewhat unique among organic acids of this strength in that their chemistry is closely linked with that of a stable tautomeric form, the parent nitroalkane. The nitro and *aci* forms share a common anion. This relationship, fundamental to nitronic acid chemistry, is illustrated with phenylnitromethane<sup>1,2,3</sup>. The equilibria of equation (1) illustrate the phenomenon of *aci*-nitro tautomerism.



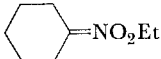
The nomenclature of nitronic acids has often been a matter of discussion<sup>4,5</sup>. The term nitronic acid (*nitronsäure*) was introduced by Bamberger<sup>6</sup>. However, use of the prefix *aci* before the nitro compound name, a concept introduced by Hantzsch a few years later<sup>7</sup>, achieved much wider use for many years. The general term *aci* was taken to mean the tautomeric, more acidic form of a *pseudo* acid. A *pseudo* acid is one whose proton is removed slowly<sup>7</sup>; a nitroalkane is a *pseudo* acid<sup>8</sup>. The prefix *iso*<sup>9</sup>, and sometimes incorrectly *pseudo*, before the nitro compound name to indicate the nitronic acid form were widely employed for many years (*isonitro* listings are found in *Chemical Abstracts* through 1946).

The nitronic acid naming system is now more widely accepted<sup>5,10</sup>. As pointed out originally by Bamberger<sup>6</sup>, and later by Hass<sup>5</sup>, it follows more closely the systematic naming of other organic acids and derivatives. It also clearly recognizes the identity of these substances as genuine organic acids. The naming of derivatives such as salts, esters, and anhydrides follows systematically. The *aci*-nitro term

employed only as a prefix<sup>11,12</sup> does not readily adapt itself to naming these derivatives.

The nitronic acid function is  $=\text{NO}_2\text{H}$ ; as a suffix it is called nitronic acid. If a prefix is required *aci*-nitro may be used<sup>11,12</sup>. For example, butane-2-nitronic acid = 2-*aci*-nitrobutane. However, the prefix nomenclature should be avoided with nitronic acids, as it is with carboxylic acids.

It is suggested that the two possible types of nitronic acids,  $\text{RCH}=\text{NO}_2\text{H}$  and  $\text{R}^1\text{R}^2\text{CH}=\text{NO}_2\text{H}$ , derived from primary and secondary nitroalkanes, be designated *primary* and *secondary* nitronic acids, respectively. Some examples of nitronic acid nomenclature follow.

$\text{CH}_3\text{CH}=\text{NO}_2\text{H}$	Ethanenitronic acid ( <i>primary</i> )
$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{H}$	Propane-2-nitronic acid ( <i>secondary</i> )
$n\text{-C}_3\text{H}_7\text{CH}=\text{NO}_2^-\text{Na}^+$	Sodium butane-1-nitronate
$\text{C}_6\text{H}_5\text{CH}=\text{NO}_2\text{CH}_3$	Methyl phenylmethanenitronate
	Ethyl cyclohexanenitronate
$\text{CH}_3\text{CH}=\text{NOCOCOCH}_3$ ↓ O	Acetic ethanenitronic anhydride
$\text{CH}_2=\text{NCl}$ ↓ O	Methanenitronyl chloride

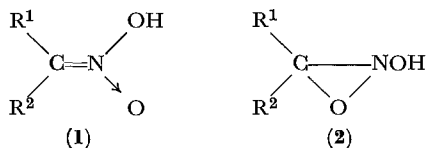
The first preparation of a nitronic acid was apparently made by Konowalow (1893)<sup>13</sup> who isolated diphenylmethanenitronic acid, mp 90°, and described it as a very unstable substance, decomposing at room temperature. The phenomenon of *aci*-nitro tautomerism in solution was discovered by Holleman (1895)<sup>14</sup>, who observed conductometrically the isomerization of 3-nitrophenylmethanenitronic acid into the nitro form. Hantzsch (1896)<sup>1</sup> was first to prepare both forms of a single nitro compound (phenylnitromethane and phenylmethanenitronic acid) and to recognize their tautomeric relationship.

The first preparation of a nitronic ester appears to be that of Nef (1894)<sup>15</sup>, who synthesized, isolated, and recognized the unstable substance  $\text{H}_2\text{NCOC}(\text{CN})=\text{NO}_2\text{C}_2\text{H}_5$ .

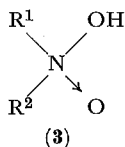
The question of nitronic acid structure was incompletely resolved and a subject of some debate and discussion for nearly 50 years after the discovery of these substances. The now accepted structure **1** was originally proposed by Nef<sup>15</sup> and employed by Bamberger<sup>6</sup>. An alternate oxazirane structure (**2**) was proposed by Hantzsch<sup>1</sup>.



Reports that certain nitronate salts possess optical activity<sup>16,17</sup>,



supporting structure **2**, were later shown to be in error<sup>18-20</sup>. Nitronate salts prepared from optically active nitroalkanes are, in fact, optically inactive<sup>19</sup>. The strong  $\pi - \pi^*$  ultraviolet absorption of nitronic acids, esters, and salts supports structure **1**. Oxaziranes do not exhibit strong ultraviolet absorption<sup>21</sup>. Unsuccessful attempts have been made to prepare substances having structure **3**, with substituents directly attached to nitrogen<sup>22</sup>.

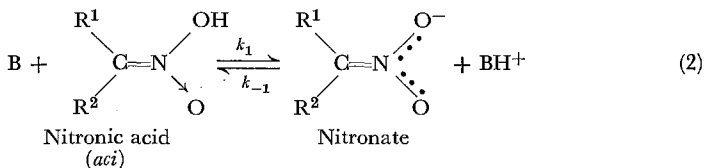


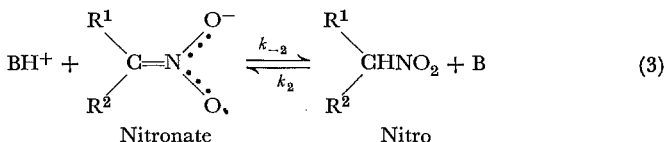
*Cis-trans* isomerism might be observed, at least in the solid state, with unsymmetrically substituted nitronic acids, analogous to the *syn* and *anti* forms of oximes. This type of isomerism has been demonstrated for nitronic esters<sup>23</sup>, nitrones<sup>24</sup>, and oximes<sup>25,26</sup>, but not for nitronic acids. It is possible that the rather stable unsymmetrical nitronic acids of wide melting range described by Hodge<sup>27</sup> are mixtures of *cis* and *trans* isomers. In solution in protic solvents such isomers would, of course, lose their identity rather rapidly.

## II. ACI-NITRO TAUTOMERISM

### A. Introduction

Study of the phenomenon of *aci*-nitro tautomerism has been, and remains, important to the development of acid-base catalysis and proton-transfer theory. The process in neutral or basic medium consists principally of equilibria involving nitronic acid (*aci* form), nitroalkane, and a common nitronate anion (equations 2, 3).





The acid-base equilibria of these equations define, to a close approximation, the ionization constants of nitronic acids ( $K_a^{\text{Aci}} = k_1/k_{-1}$ ) and nitroalkanes ( $K_a^{\text{Nitro}} = k_2/k_{-2}$ ) where B is a solvent molecule (water, ethanol). Tautomerization involving ketonitronic acids is discussed in section III.C.4.

Many kinetic studies of *aci*-nitro tautomerism, employing diverse methods, have been made. The earliest studies<sup>14,28,34</sup>, which employed conductivity measurements, made use of the much greater conductivity of the *aci* form, due to its greater dissociation into nitronate anion. Other methods have taken advantage of various properties of the *aci* form not observed in the nitro form, such as: rapid reaction with bromine (titration)<sup>35-37</sup>, failure to be reduced polarographically<sup>38-49</sup>, and strong ultraviolet absorption<sup>50-53</sup>. These studies have included rate measurements of forward and reverse processes.

In retrospect, an interesting aspect of many rate studies was the failure, even until recent times, to recognize the hybrid structure of the nitronate anion intermediate<sup>29,30,38</sup>. Confusion exists in many earlier papers relating to nitronate anions having different 'structures' (with negative charge on carbon or oxygen<sup>38</sup>, or possessing optical activity<sup>16</sup>), and giving validity to these structures in kinetic and mechanistic expressions<sup>38</sup>. Present theory allows only *one* structure for the mesomeric nitronate anion, with negative charge delocalized principally on oxygen.

### B. Tautomerization of Nitronic Acids to Nitroalkanes

The tautomerization of a nitronic acid to its parent nitroalkane (equations 2 and 3) proceeds essentially to completion for most simple nitroalkanes because of the relatively weaker acidity of a nitroalkane compared to its corresponding nitronic acid (*aci* form). The kinetics of tautomerization of the *aci* to the nitro form has been studied extensively, principally in water solvent. Early conductometric studies of Holleman<sup>14,54</sup> and Hantzsch<sup>32,33</sup> showed the process to be very rapid.

Proton removal from nitronic acid oxygen ( $k_1$ ) has been measured for phenylmethanenitronic acid ( $k_1 = 4.14 \times 10^{-5}$  l/mole-sec in

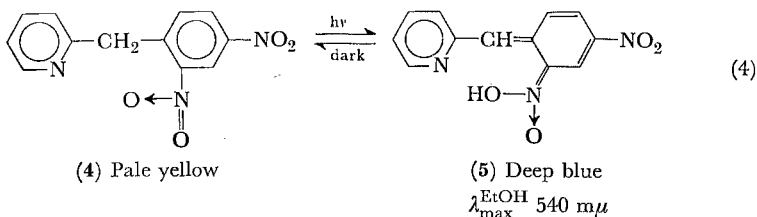
99.5 % water, 0.5 % ethanol at 25°). From the ionization constant in water,  $K_a^{Aci} = 1.3 \times 10^{-4}$ <sup>34,39,55</sup>, the reverse process, protonation on oxygen, may be calculated to be much faster ( $k_{-1} = 3.2 \times 10^{-1}$ /mole-sec).

Many more measurements have been made of the overall rate of tautomerization of the nitronic acid to the nitro form (protonation on carbon). One may assume a steady-state expression and define this rate as  $K_a^{Aci} k_{-2}$  since  $k_{-2}$  is slow compared to  $k_{-1}$ . Table 1 summarizes the available rate data. From the  $K_a^{Aci}$  values the rate of protonation on carbon,  $k_{-2}$ , may be calculated.

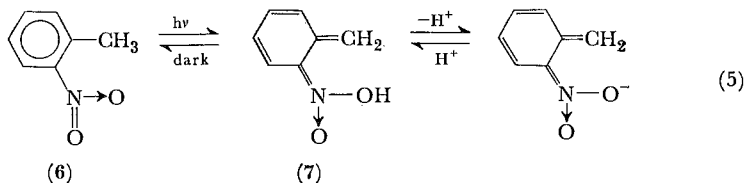
The mechanism of the tautomerization process expressed in equations (2) and (3) requires that C-protonation occurs on the intermediate nitronate anion, not on the nitronic acid or some other species. In agreement with this postulate is the fact that the tautomerization rate is accelerated in slightly basic solution, inhibited in acid solution<sup>51,65</sup>. Strong nitronic acids which are highly ionized, such as bromomethanenitronic, tautomerize extremely rapidly<sup>32,47</sup>. Highly hindered acids of the type  $R_3CC(C_6H_5)=NO_2H$  do not tautomerize at a measurable rate in acid solution, but require a basic catalyst to increase the concentration of nitronate ion, thus permitting tautomerization to occur readily<sup>65</sup>.

Tautomerization does occur in acid solution<sup>44</sup>, but strong acid suppresses ionization and usually favors other reactions such as the Nef. Armand<sup>47</sup> found acids  $XCH=NO_2H$ ,  $X_2C=NO_2H$ , and  $CH_3CX=NO_2H$  ( $X = Cl, Br$ ) to tautomerize rapidly and completely without undergoing Nef reaction, even at low pH. On the other hand, with *d*-2-nitrooctane acid-catalyzed Nef reaction (in *N* hydrochloric acid at 100°) to form 2-octanone occurred more rapidly than tautomerization since it was observed that the recovered unreacted nitro compound retained all its optical activity<sup>50</sup>.

A different mechanism involving direct proton transfer to carbon from a nitronic acid intermediate (rather than a nitronate anion) is involved in the much-studied dark reaction of tautomerization of compounds such as arylmethanenitronic acids to the nitro compound (e.g. **5**  $\rightarrow$  **4**)<sup>66-72</sup> (equation 4). Nitronic acids identical with those formed photochemically can also be formed by acidification of the alkali metal salts<sup>73</sup>. The presence of a nitro group *ortho* of the methylene group is required for the photochromic transformation<sup>74-78</sup>. The pyridyl group in **4** may be replaced by phenyl<sup>75</sup>, alkyl<sup>78</sup>, or hydrogen<sup>71</sup>. The reaction is not limited to solutions, but occurs also in the solid state where it was first observed<sup>67,79,80</sup>.



The direct intramolecular proton transfer mechanism involving a nitronic acid is supported by several facts, in addition to the requirement of an *ortho* nitro group. The dark reaction rate [*Aci* (5)  $\rightarrow$  Nitro (4)] is accelerated in acid solution<sup>81</sup>. It is also faster in an aprotic solvent such as isooctane than in a protic solvent (ethanol) by a factor of ca  $10^4$ <sup>66</sup>. The rate is strongly *accelerated* by electron-releasing groups; replacing  $\text{NO}_2$  by  $\text{NH}_2$  in **5** increases the rate ca  $10^4$ <sup>82</sup>. A large negative entropy ( $-45$ – $50$  eu) supports a rigid transition state<sup>75,82</sup>. The intramolecular nature of the process was demonstrated in a very simple system. Deuterium is incorporated into *o*-nitrotoluene (**6**)—but not *p*-nitrotoluene under the same conditions—when irradiated in deuterium oxide-dioxane<sup>71,76–78</sup>. Ionization of the nitronic acid (**7**) provides a facile deuterium exchange mechanism (equation 5).



The effect of structure on the overall rate of tautomerization of nitronic acids to the nitro form (rate =  $K_a^{\text{Aci}} k_{-2}$ ) is determined by the two factors in this expression—the ionization constant of the nitronic acid,  $K_a^{\text{Aci}}$ , and the rate of C-protonation of the anion ( $k_{-2}$ ). The constant  $k_{-2}$  may be evaluated from the above rate expression if  $K_a^{\text{Aci}}$  is known, or, if  $K_a^{\text{Nitro}}$  and the uncatalyzed rate of proton removal from the nitroalkane ( $k_2$ ) are known,  $k_{-2}$  may be calculated from the equilibrium expression  $K_a^{\text{Nitor}} = k_2/k_{-2}$ . The available data are summarized in Table 1. Structural factors which affect  $K_a^{\text{Aci}}$  and  $k_{-2}$  are germane to the general problem of anion stability.

Inductive effects may be compared by examining those nitronic acids not exhibiting large resonance or other anion-stabilizing

TABLE I. Rates of tautomerization of nitronic acids to nitroalkanes.

No.	Nitronic acid	Temp. (°C)	Solvent aqueous	$K_a^{Aci} \times 10^4$		$k_{-2}$ (l/mole-min)	log $k_{-2}$	$K_a^{Aci} k_{-2}$ (l/mole-min)	log $K_a^{Aci} k_{-2} + 2$	Ref.
				$K_a^{Aci}$	$pK_a^{Aci}$					
$  \begin{array}{c}  R^1 \\  \diagdown \\  C=NO_2H \\  \diagup \\  R^2  \end{array}  \xrightleftharpoons[k_{-1}]{k_1}  \begin{array}{c}  R^1 \\  \diagdown \\  C=NO_2^- + H^+ \\  \diagup \\  R^2  \end{array}  \xrightleftharpoons[k_2]{k_{-2}}  \begin{array}{c}  R^1 \\  \diagdown \\  CHNO_2 \\  \diagup \\  R^2  \end{array}  $ $K_a^{Aci} = k_1/k_{-1}$										
1.	$O_2NCH=NO_2H$	25	H <sub>2</sub> O	140	1.86	$1.9 \times 10^5$	5.28	2600	5.42	32, 56
2.	$CH_2=NO_2H$	25	H <sub>2</sub> O	5.6	3.25	$4.1 \times 10^4$	4.61	23	3.36	29-32, 56
3.	$CH_3CH=NO_2H$	25	H <sub>2</sub> O	0.40	4.4	$9.0 \times 10^2$	2.95	0.036	0.55	32, 56, 57
4.	$CH_3CH_2CH=NO_2H$	25	EtOH, 85%	0.25 <sup>a</sup>	4.6 <sup>a</sup>	$4.5 \times 10^{3a}$	3.65 <sup>a</sup>	0.076	0.88	36, 42,
5.	$CH_3(CH_2)_5C(CH_3)=NO_2H$	25	EtOH, 85%	(0.05) <sup>b</sup>	(5.3) <sup>b</sup>	$(6 \times 10^2)^b$	(2.8) <sup>b</sup>	0.0031	-0.51	52, 58-60
6.	$2-BrC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.042	0.62	50, 52
7.	$3-BrC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.028	0.45	61
8.	$4-BrC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.018	0.25	61
9.	$2-ClC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.032	0.50	61
10.	$3-ClC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.025	0.40	61
11.	$4-ClC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.014	0.15	61, 62
12.	$2-O_2NC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	(0.15) <sup>b</sup>	1.18	61, 63
13.	$3-O_2NC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.092	0.96	61, 63
14.	$4-O_2NC_6H_4CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.11	1.04	61, 63
15.	$C_6H_5CH=NO_2H$	0	EtOH, 50%	—	—	—	—	0.0056	-0.25	61, 63
		25	H <sub>2</sub> O	1.3	3.9	$(1 \times 10^3)^b$	(3.0) <sup>b</sup>	0.0050	-0.30	34, 36, 39,
								(0.125) <sup>b</sup>	(1.1) <sup>b</sup>	53, 55, 64

16.	$O_2NCH_2CH_2CH=NO_2H$	25	EtOH, 85%	32	2.49	$1.7 \times 10^2$	2.23	0.55	1.74	52
17.	$O_2NCH_2(CH_2)_2CH=NO_2H$	25	EtOH, 85%	2	3.70	$4.6 \times 10^2$	2.66	0.093	0.97	52
18.	$O_2NCH_2(CH_2)_3CH=NO_2H$	25	EtOH, 85%	1.6	3.80	$1.28 \times 10^3$	3.11	0.204	1.31	52
19.	$O_2NCH_2(CH_2)_4CH=NO_2H$	25	EtOH, 85%	1.4	3.85	$1.14 \times 10^3$	3.06	0.159	1.20	52
20.	$O_2NCH(CH_2)_2C=NO_2H$	25	EtOH, 85%	2.8	3.55	$1.6 \times 10^2$	2.20	0.044	0.64	52
21.	$\begin{array}{c} CH_3OH \quad CH_2OH \\   \quad   \\ O_2NCH(CH_2)_3C=NO_2H \end{array}$	25	EtOH, 85%	0.22	4.66	$2.95 \times 10^3$	3.47	0.065	0.81	52
22.	$\begin{array}{c} CH_3OH \quad CH_2OH \\   \quad   \\ O_2NCH(CH_2)_2C=NO_2H \end{array}$	25	EtOH, 85%	1.0	4.00	$1.64 \times 10^3$	3.22	0.164	1.21	52
23.	$\begin{array}{c} CH_3OCH_2CH_2OCH_3 \\   \\ HO_2N=CHCH_2CH=NO_2H^c \end{array}$	25	EtOH, 85%	112	1.95	$1.28 \times 10^3$	3.11	14.5	3.16	52
24.	$HO_2N=CH(CH_2)_2CH=NO_2H^c$	25	EtOH, 85%	5.0	3.30	$1.86 \times 10^3$	3.28	0.93	1.97	52
25.	$HO_2N=CH(CH_2)_3CH=NO_2H^c$	25	EtOH, 85%	3.5	3.46	$2.91 \times 10^3$	3.46	1.02	2.01	52
26.	$HO_2N=CH(CH_2)_4CH=NO_2H^c$	25	EtOH, 85%	2.8	3.55	$1.04 \times 10^3$	3.02	0.29	1.46	52
27.	$HO_2N=C(CH_2)_2C=NO_2H^c$	25	EtOH, 85%	7.1	3.15	$3.56 \times 10^3$	3.55	2.53	2.40	52
28.	$\begin{array}{c} CH_3OH \quad CH_2OH \\   \quad   \\ HO_2N=C(CH_2)_3C=NO_2H^c \end{array}$	25	EtOH, 85%	0.5	4.30	$9.4 \times 10^3$	3.97	0.47	1.67	52
29.	$\begin{array}{c} CH_3OH \quad CH_2OH \\   \quad   \\ HO_2N=C(CH_2)_2C=NO_2H^c \\   \\ CH_3OCH_2CH_2OCH_3 \end{array}$	25	EtOH, 85%	2.5	3.60	$11.3 \times 10^3$	4.06	2.82	2.45	52

<sup>a</sup> Data in water (reference 42).

<sup>b</sup> Values in parentheses are estimated; cf. reference 56.

<sup>c</sup> Data not corrected for statistical factor.

effects. Of these, the strongest acids tautomerize at the fastest rate as shown in Figure 1. The acids which tautomerize at the fastest rate also have the fastest C-protonation rate ( $k_{-2}$ ) as shown in

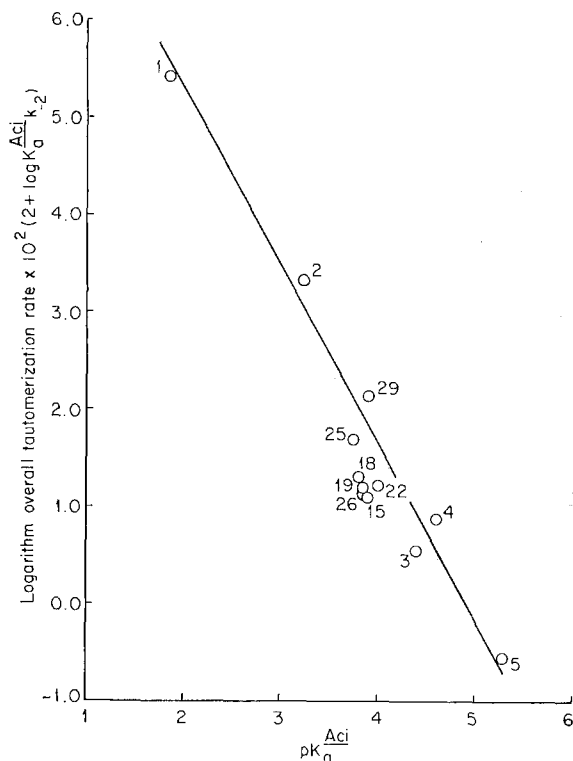


FIGURE 1. Plot of logarithm of overall rate of tautomerization of nitronic acids to nitroalkanes  $\times 10^2 (2 + \log K_a^{Aci} k_{-2})$  vs.  $pK_a^{Aci}$ ; data at  $25^\circ$  in Table 1. Data for bisnitronic acids have been corrected for statistical factor.

Figure 2. Hantzsch<sup>32</sup> reported bromomethanenitronic and nitromethanenitronic acids to tautomerize at rates much too rapid to measure compared to methanenitronic, the weaker acid. Armand<sup>47</sup> observed only instantaneous tautomerization, even at low pH (no Nef reaction), with the strong acids  $X_2C=NO_2H$ ,  $XCH=NO_2H$  and  $CH_3CX=NO_2H$  ( $X = Cl, Br$ ). *m*-Nitrophenylmethanenitronic acid tautomerizes to the nitro form ca 20 times faster than the weaker phenylmethanenitronic acid.

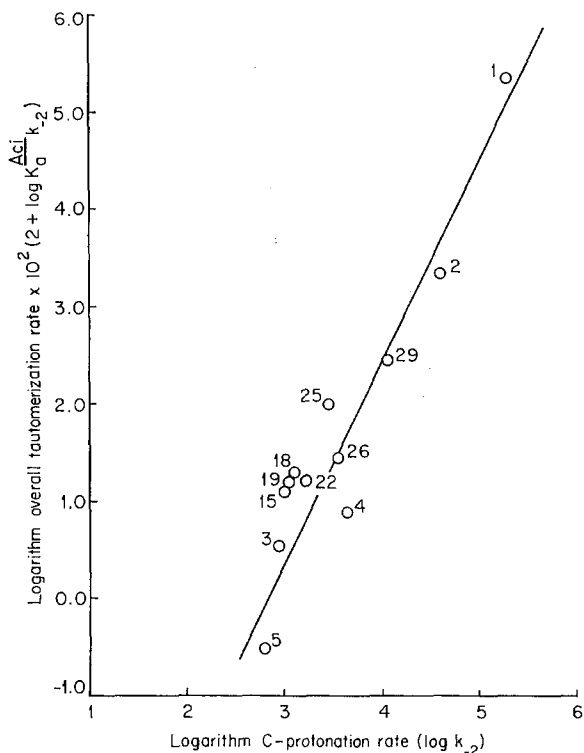


FIGURE 2. Plot of logarithm of overall rate of tautomerization of nitronic acids to nitroalkanes  $\times 10^2 (2 + \log K_a^{Aci} k_{-2})$  vs. logarithm of C-protonation rate ( $\log k_{-2}$ ); data at  $25^\circ$  in Table 1.

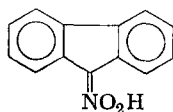
Inductive effects exhibit predictable behavior in relation to ionization constants, which affect tautomerization rates. Electron-withdrawing groups such as halogen and nitro increase  $K_a^{Aci}$  (see Table 5 in section II.D), and tautomerization rate. Electron-releasing groups such as methyl decrease  $K_a^{Aci}$  and tautomerization rate. For example, ethanenitronic acid tautomerizes ca  $10^3$  times more slowly than the stronger methanenitronic acid;  $\alpha$ -phenylpropanenitronic acid tautomerizes more slowly than  $\alpha$ -phenylethanenitronic acid<sup>83</sup>.

On the other hand, the increase in C-protonation rate caused by substitution of electronegative groups on the nitronate carbon (Figure 2) is opposite to what one might expect. An electron-withdrawing group lowers electron density at the nitronate carbon and should slow C-protonation. One possible explanation may be

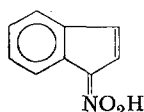


the presence of a polar, negative field very close to the nitronate carbon; thus protons are readily attracted to the site. However, when the electronegative group is moved away from the nitronate carbon, as in the series of  $\omega$ -nitronalkanenitronic acids  $O_2N(CH_2)_nCH=NO_2H$ , one observes expected behavior<sup>52</sup>. The overall tautomerization rate decreases with increasing chain length;  $K_a^{Aei}$  decreases also, and the C-protonation rate increases slightly (Table 1).

Slow tautomerization of nitronate anions to the nitro form is observed for those anions having ground state energies very much lower than the parent nitro compound. For example, certain resonance-stabilized nitronate anions may show this property. The nitro forms of fluorene-9-nitronic acid (**8**)<sup>84,85</sup> and indene-1-nitronic acid (**9**)<sup>86</sup> can be prepared only in aprotic solvents<sup>85a</sup>. Fluorene-9-nitronic acid (**8**) is very stable<sup>84</sup>. 2,4-Cyclopentadiene-1-nitronic acid is very unstable<sup>86a</sup>. Its sodium salt on acidification, produces



(8)



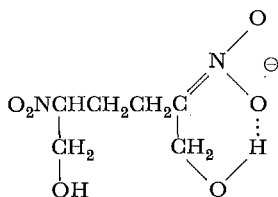
(9)

a black polymer and 1-nitro-1,3-cyclopentadiene<sup>86a</sup>. Phenylmethanenitronic and methanenitronic acids are of comparable acid strength ( $pK_a^{Aei}$  3.9 and 3.25, respectively), but phenylmethanenitronic acid tautomerizes approximately 100 times more slowly (Table 1). Resonance-stabilized nitronic acids which tautomerize slowly do so principally because the C-protonation rate is relatively slow. There is a rather large activation energy barrier between the anion and the nitro form.

Resonance stabilization of a nitronate anion often increases acid strength which may sometimes actually account for a slight enhancement of overall tautomerization rate. For example, a 20% increase in tautomerization rate is observed for 4-nitrophenylmethanenitronic acid relative to the 3-nitro isomer<sup>61</sup>; the 4-bromo and 4-chloro isomers tautomerize more slowly than their corresponding *meta* isomers<sup>61</sup>. However, the most usual consequence of significant nitronate anion stabilization relative to the nitro form appears to be a decrease, rather than an increase, in overall tautomerization rate.

Stabilization of nitronate anions by hydrogen bonding also results in an increase in  $K_a^{Aei}$  and a decrease in C-protonation rate. The

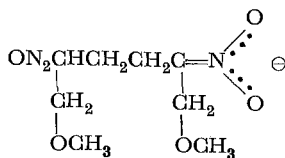
methylol derivative **10** is a somewhat stronger acid than the corresponding methyl ether (**11**)<sup>52</sup>. But, the *overall* tautomerization rate ( $K_a^{Aci} k_{-2}$ ) of the hydrogen-bonded acid (**10**) is about 4 times slower, despite the greater acidity. This is due to the slower C-protonation



(10)

$$pK_a^{Aci} 3.55$$

$$k_{-2} = 1.6 \times 10^{-2} \text{ min}^{-1}$$



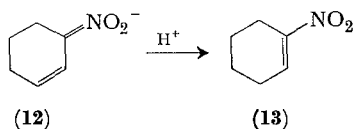
(11)

$$pK_a^{Aci} 4.00$$

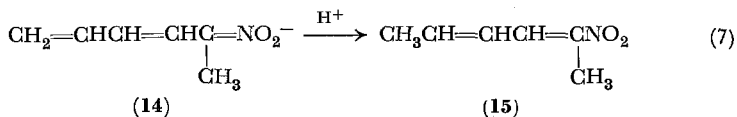
$$k_{-2} = 16.4 \times 10^{-2} \text{ min}^{-1}$$

rate (10 times slower). A similar effect is observed with the butane-1,4-bisnitronic acid derivatives of **10** and **11** (data in Table 1). The failure of certain hydroxynitronic acids (including **10**) to undergo a Nef reaction may be caused by their hydrogen-bonded, stabilized nitronate anions (see discussion in section III.C.1.a).

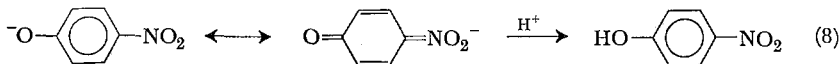
Rapid tautomerization of nitronate anions to the nitro form is observed with anions which do not differ much in ground state energy from the parent nitro compound. The nitronic acid forms are extremely unstable and are rarely isolated. Conjugated anions derived from conjugated nitroolefins, nitrodienes, and nitro aromatic compounds protonate rapidly. C-protonation usually occurs most rapidly at the terminal position of these nitronate anions and often favors the conjugated nitroolefin product under kinetic control. For example, anion **12** rapidly protonates at the terminal 3-position to yield 1-nitrocyclohexene (**13**) exclusively (equation 6) apparently without intervention of non-conjugated 3-nitrocyclohexene<sup>58</sup>; this protonation is very rapid and occurs at about the same rate as that for propane-1-nitronate to 1-nitropropane<sup>52,58</sup>. Conjugated nitronate anion **14** protonates at the terminal 5-position to yield only nitroolefin **15**<sup>58</sup> (equation 7).



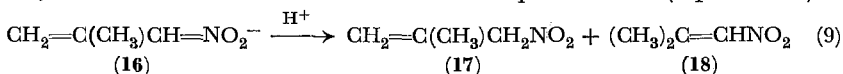
(6)



Protonation of nitronates derived from aromatic nitro compounds occurs very rapidly, also at a terminal position (equation 8).

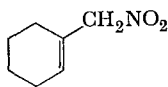


Protonation can occur under kinetic control to yield some of the unconjugated nitroolefin, as in the protonation of nitronate anion **16**; a 1:1 mixture of olefins **17** and **18** is produced<sup>10</sup> (equation 9).

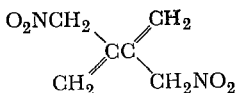


The equilibrium composition of nitroolefins is a matter of interest and has received some study<sup>10,87-91</sup>. As with olefinic ketones and other unsaturated carbonyl compounds the  $\alpha,\beta$ -unsaturated isomer is usually favored, and the position of equilibrium is affected by structure and solvent<sup>87</sup>. Nitrobenzenes and olefins such as **13** and **15** are favored. Thermodynamically, conjugated isomer **18** is favored over **17** by 4:1<sup>10,87</sup>; but, olefin  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{NO}_2$  is favored 100% over  $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{NO}_2$ <sup>87</sup>.

Exceptional behavior is exhibited by certain olefins substituted with a nitromethyl group,  $\text{CH}_2\text{NO}_2$  (note **17**, above). The  $\beta,\gamma$ -isomer is often favored at equilibrium as, for example, with olefins **19**<sup>10,88</sup>, **20**<sup>89,90</sup>, and **21**<sup>91</sup>. The product composition of nitroolefins



(19)



(20)

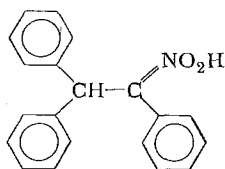


(21)

derived from the nitronate anions of **19**, **20**, and **21** under kinetic control is not known.

Slow tautomerization is observed with certain nitronic acids highly substituted about the nitronate carbon. Quantitative data are limited. Octane-2-nitronic acid tautomerizes 25 times more slowly than propane-1-nitronic acid<sup>52</sup>. Nitronic acids such as **22**<sup>65</sup> tautomerize much more slowly than phenylmethanenitronic acid<sup>1</sup>.

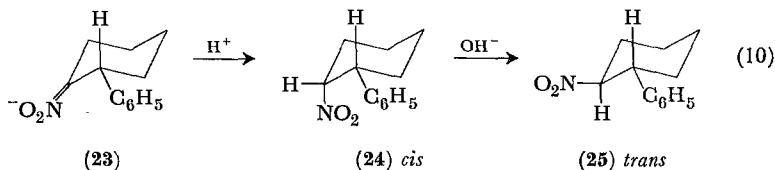
These results indicate that a slow rate of C-protonation of the



(22)

nitronate anion is believed to be a factor, a result of poor solvation about the nitronate carbon.

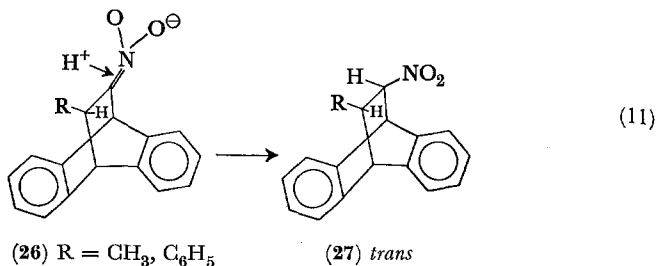
The stereochemistry of *aci*-nitro tautomerism has been studied in a few systems. In simple monocyclic nitronate anions with vicinal substituents one observes kinetic preference for protonation from the least hindered side; this result leads to the least stable product (steric approach control). Protonation of 2-phenylcyclohexanenitronate ion (**23**) leads to 98% *cis*-2-phenyl-1-nitrocyclohexane



(**24**, axial nitro); equilibration with alkali leads to 99% of the *trans* (equatorial nitro) isomer (**25**)<sup>92</sup> (equation 10). Similar results are found in certain steroids (kinetic preference for axial nitro)<sup>93,94</sup>. (A controversy exists relating to the configuration of **23**—whether the phenyl group is axial or equatorial in the protonation transition state<sup>92,95,96</sup>.) In cyclohexane systems, in the absence of vicinal substituents, there is a kinetic<sup>92a</sup> as well as equilibrium preference for equatorial nitro (ca 80–90%) over axial<sup>93,94,97–104</sup>. For example, 4-*t*-butylcyclohexanenitronate protonates under kinetic control to yield 76% *trans*-4-*t*-butylnitrocyclohexane (equatorial nitro)<sup>92a</sup>. Equilibration of 1,3- and 1,4-dinitrocyclohexanes in ethanolic sodium bicarbonate leads to the diequatorial isomers (ca 80–90%)<sup>103</sup>.

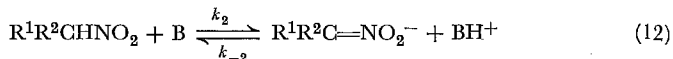
In the rigid bicyclic system **26**, protonation with dilute acetic acid occurs with 84–97% kinetic preference for the most stable, *trans* product (**27**)<sup>105,106</sup> (equation 11). Proton approach is *cis* to the vicinal R group (product development control). In this more rigid

system, eclipsing of incipient nitro and neighboring R group results in a higher energy transition state than in the more flexible cyclohexane ring system.



### C. Proton Removal from Nitroalkanes

Removal of a proton from a nitroalkane produces a nitronate anion (reverse of equation 3) (equation 12). This reaction occurs in the reverse of *aci*-nitro tautomerism and has been studied extensively; it proceeds at a convenient rate at ordinary temperatures



and is easily followed for kinetic measurements. The reaction of proton removal, as well as protonation of nitronate anions, is subject to general acid-base catalysis<sup>40,107-110</sup>. Rate measurement in various buffer solutions of different bases gives good Brönsted plots (Figure 3)<sup>40,109,111,111a</sup>. However, dimethyl and trimethylamine show poor correlation of amine base strength with neutralization rates of nitroethane<sup>112</sup>; the discrepancy has been attributed to steric factors<sup>111a,112</sup>.

The rates of uncatalyzed proton removal from various nitroalkanes determined in water solvent are summarized in Table 2. Also included are rates of reprotonation (C-protonation) and ionization constants ( $K_a^{\text{Nitro}}$ ). As noted by Bell (reference 107, p. 160) an expected linear relationship is observed between acid strength of the nitroalkane and rate of proton removal (Figure 4). The nitroalkanes of greatest acidity ionize most rapidly.

The energy of activation for proton removal with water as a base is ca. 20-23 kcal/mole<sup>57,119</sup>. A relatively large negative entropy of activation is observed (-19-24 eu for nitroalkanes<sup>28,42,57,112,119</sup>). For other bases (amines, hydroxide, and acetate ion) the energy of activation is less (12-16 kcal/mole) and the entropy of activation

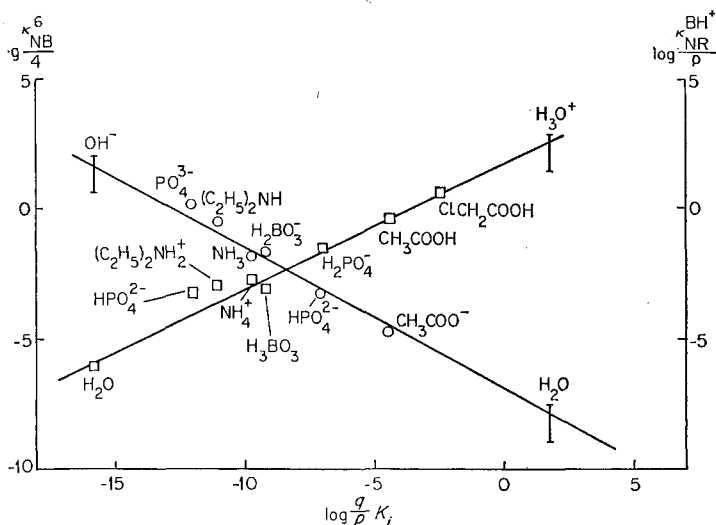
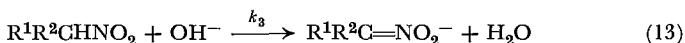


FIGURE 3. Dissociation and recombination rates of the nitro-form of 1-nitropropane as a function of the dissociation constant of the acting acid or of the acid conjugated with the acting base:  $\square$  recombination of nitro-form,  $\circ$  dissociation of the nitro-form. [Reproduced, by permission, from ref. 40.]

more positive ( $-7$ – $16$  eu)<sup>92a,111,112,120</sup>. These data agree with a slow proton removal process requiring a large amount of solvent reorganization in the transition state<sup>121</sup>.

Base-catalyzed proton removal from nitroalkanes is an important reaction (equation 13). In kinetic studies solutions of sodium hydroxide in water, aqueous dioxane or aqueous ethanol have been fre-

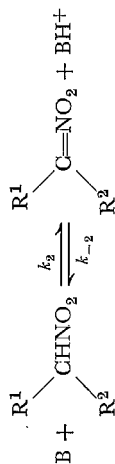


quently employed. Reaction rate data are summarized in Table 3. Hantzsch<sup>32</sup> made the first studies with nitroethane employing a conductometric method.

Junell<sup>37,130–132</sup>, and later Pedersen<sup>133</sup>, made the first thorough kinetic investigations of proton removal from nitroalkanes employing acetate catalyst and bromine titration of the nitronate anion formed. They demonstrated that the bromine and chlorine reaction rates are identical, that the rate-limiting step is proton removal, and that the reaction is first order in nitro compound and base. Pearson and Dillon showed bromine and iodination rates to be identical<sup>57</sup>.

Deuterium substitution in nitroalkanes results in a slower reaction rate; for hydroxide ion an isotope effect of  $7.4$ – $10.3$  is observed<sup>111,120</sup>.

TABLE 2. Rates of ionization of nitroalkanes in water at 25°.



Nitroalkane	$K_a^{\text{Nitro}} (k_2/k_{-2})$	$pK_a^{\text{Nitro}}$	$k_{-2}$ (1/mole-min)	$k_2$ (1/mole-min)	$\log k_2$	Ref.
$\text{CH}_3\text{NO}_2$	$6.1 \times 10^{-11}$	10.21	$4.1 \times 10^4$	$2.5 \times 10^{-6}$	-5.60	28, 37, 56, 59, 113
$\text{CH}_3\text{CH}_2\text{NO}_2$	$3.2 \times 10^{-9}$	8.5	$9.0 \times 10^2$	$2.9 \times 10^{-6}$	-5.54	32, 47, 56, 59, 60, 114
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	$1.05 \times 10^{-9}$	8.98	$4.5 \times 10^3$	$4.7 \times 10^{-6}$	-5.33	42, 60, 115
$\text{O}_2\text{N}(\text{CH}_2)_6\text{NO}_2$	$(10^{-10})^a$	$(10.3)^b$	$1.0 \times 10^3$	$(10^{-7})$	(-7)	52, 116
$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CH}_3)\text{NO}_2$	$(10^{-10})^a$	(10)	$(6 \times 10^2)$	$(6 \times 10^{-8})$	(-7.2)	50, 52, 116
$\text{CH}_2\text{BrNO}_2$	$5 \times 10^{-9}$	8.3	$1.6 \times 10^5$	$8 \times 10^{-4}$	-3.1	37, 47, 56
$\text{CH}_2(\text{NO}_2)_2$	$2.7 \times 10^{-4}$	3.57	$1.9 \times 10^5$	50	1.7	32, 56, 117, 118
$\text{CH}_3\text{CHClNO}_2$	$1.3 \times 10^{-7}$	6.9	$2.6 \times 10^2$	$3.4 \times 10^{-5}$	-4.47	47, 56
$\text{CH}_3\text{COCH}_2\text{NO}_2$	$2.3 \times 10^{-5}$	4.64	$8.0 \times 10^6$	2.2	0.35	56
$\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$	$1.6 \times 10^{-7}$	6.8	$1.9 \times 10^4$	$3 \times 10^{-3}$	-2.5	34, 38, 39, 53, 55

<sup>a</sup> Values in parentheses are estimated from available data in references cited.

<sup>b</sup> Corrected for statistical factor.

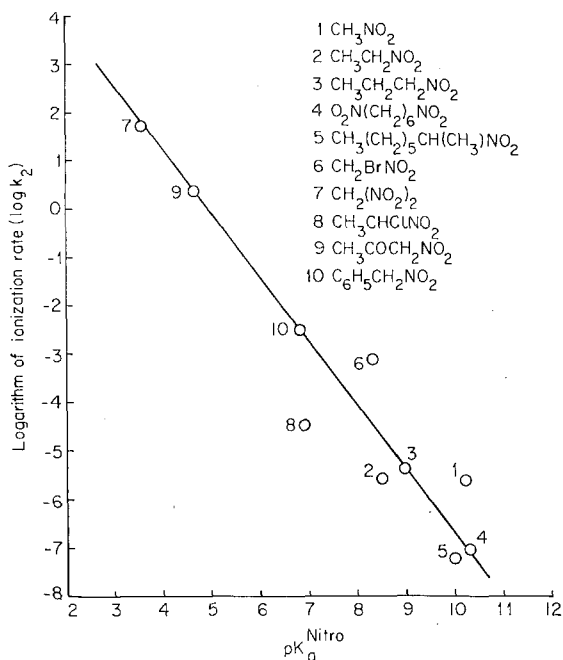


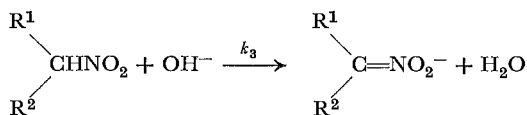
FIGURE 4. Plot of logarithm of ionization rate ( $\log k_2$ ) of nitroalkanes in water at  $25^\circ$  vs.  $pK_a^{\text{Nitro}}$ ; data at  $25^\circ$  in Table 2.





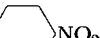

The isotope effect varies with the  $pK_a$  difference of the reacting systems<sup>111,134-136</sup>. The rate of neutralization of nitroalkanes is faster in  $\text{D}_2\text{O}$ <sup>127</sup> and in aprotic solvents<sup>121,126</sup> than in water. Hindrance in the attacking base (e.g. collidine) results in a relatively slower rate of proton removal<sup>111,112,135-138</sup>.

The effect of structure on rates of proton removal may be seen from the data in Tables 2 and 3, and Figure 4. It has been pointed out by Bordwell<sup>92a</sup> that the transition state for proton abstraction resembles the ground state rather than nitronate ion; inductive and steric effects are the important factors which affect rate of proton removal. Thus electron-withdrawing groups such as nitro enhance the rate<sup>32,57,139</sup>. Rates of neutralization of substituted phenylnitromethanes indicate a 50-fold rate acceleration by *p*-nitro (relative to hydrogen)<sup>120</sup>. The substitution by electron-releasing *p*-methyl decreases the rate by one-half<sup>120</sup>. Bulky substituents about the acidic proton decrease the rate; 2-nitrobutane reacts ca. 25 times more






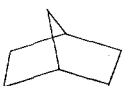
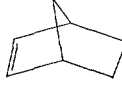
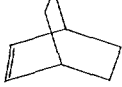
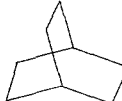


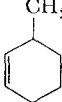
TABLE 3. Rates of neutralization of nitroalkanes by hydroxide ion.



No.	Nitroalkane	Temp. (°C)	Solvent	$k_3$ (l/mole-min)	Ref.
1.	$\text{CH}_3\text{NO}_2$	25	$\text{H}_2\text{O}$	1026	110, 122
				1600	111
		0	$\text{H}_2\text{O}$	173	123
				237	28
2.	$\text{CH}_3\text{CH}_2\text{NO}_2$	25	$\text{H}_2\text{O}$	236	122
				312	111
				336	124
				354	110, 125, 126
		0	$\text{H}_2\text{O}$	35	123
				37.5	127
3.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	25	$\text{H}_2\text{O}$	39	28
		25	$\text{H}_2\text{O}$	195	110, 122
		0	$\text{H}_2\text{O}$	29	123
4.	$(\text{CH}_3)_2\text{CHNO}_2$	25	$\text{H}_2\text{O}$	16.4	110, 122
		0	$\text{H}_2\text{O}$	19	111
				2	28, 123
				19.2	92a
		25	$\text{CH}_3\text{OH}^a$	19.2	92a
5.	$n\text{-C}_3\text{H}_7\text{CH}_2\text{NO}_2$	25	$\text{H}_2\text{O}$	192	122
6.	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NO}_2$	25	$\text{H}_2\text{O}$	8.8	122
7.	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{NO}_2$	25	$\text{CH}_3\text{OH}^a$	27.6	92a
8.		0	1:1 Dioxane- $\text{H}_2\text{O}$	No reaction	120
9.		0	1:1 Dioxane- $\text{H}_2\text{O}$	165	120
10.		0	1:1 Dioxane- $\text{H}_2\text{O}$	39.8	120
11.		28	1:1 Dioxane- $\text{H}_2\text{O}$	78.3	120
		0	1:1 Dioxane- $\text{H}_2\text{O}$	7.62	120
		25	$\text{H}_2\text{O}$	21.4	111, 128
		25	$\text{CH}_3\text{OH}^a$	19.8	92a
		25	$\text{CH}_3\text{OH}^a$	<i>cis</i> 60 <i>trans</i> 12	92a
12.	$t\text{-C}_4\text{H}_9$ 	25	$\text{CH}_3\text{OH}^a$	<i>cis</i> 114 <i>trans</i> 0.56	92a
13.	 $\text{C}_6\text{H}_4\text{-4-Cl}$	25	$\text{CH}_3\text{OH}^a$	<i>cis</i> 114 <i>trans</i> 0.56	92a

(continued)

TABLE 3—continued

No.	Nitroalkane	Temp. (°C)	Solvent	$k_3$ (1/mole-min)	Ref.
14.	 <chem>C6H4-2-CH3</chem>	25	<chem>CH3OH^a</chem>	<i>cis</i> 60 <i>trans</i> 0.28	92a
15.		0	1:1 Dioxane- <chem>H2O</chem>	20.6	120
16.		0	1:1 Dioxane- <chem>H2O</chem>	16.0	120
17.		0	1:1 Dioxane- <chem>H2O</chem>	<i>endo</i> 134 <i>exo</i> 6.8	120
18.		0	1:1 Dioxane- <chem>H2O</chem>	<i>endo</i> 210 <i>exo</i> 7.86	120
19.		0	1:1 Dioxane- <chem>H2O</chem>	<i>endo</i> 50.6 <i>exo</i> 47.2	120
20.		0	1:1 Dioxane- <chem>H2O</chem>	37.9	120
21.		0	1:1 Dioxane- <chem>H2O</chem>	21.4	120
22.	 <chem>C6H4-3-OCH3</chem>	25	<chem>EtOH</chem> , 37%	(0.022) <sup>b,c</sup>	129
23.	 <chem>C6H4-3-OCH3</chem>	25	<chem>EtOH</chem> , 37%	0.0069 <sup>b</sup>	129
24.	<chem>3-O2NC6H4CH2NO2</chem>	0	1:1 Dioxane- <chem>H2O</chem>	2110	120
25.	<chem>4-O2NC6H4CH2NO2</chem>	0	1:1 Dioxane- <chem>H2O</chem>	4560	120
26.	<chem>C6H5CH2NO2</chem>	0	1:1 Dioxane- <chem>H2O</chem>	92.8	120
27.	<chem>4-CH3C6H4CH2NO2</chem>	0	1:1 Dioxane- <chem>H2O</chem>	51.9	120

<sup>a</sup> Sodium methoxide base.<sup>b</sup> Stereochemistry not established.<sup>c</sup> Estimated from data in 27% EtOH reported in ref. 129.

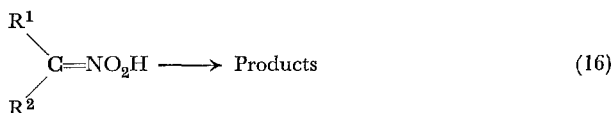
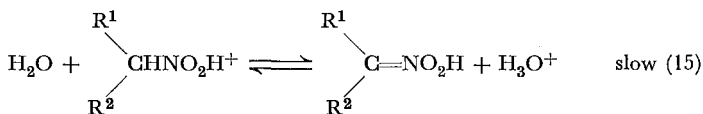
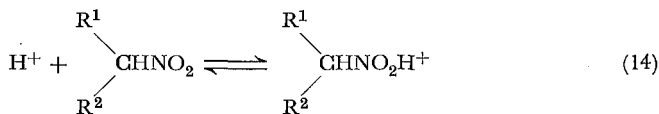
slowly than nitroethane<sup>122</sup>. 3-Ethyl-5-(3-methoxyphenyl)-4-nitrocyclohexene<sup>129</sup> (Table 3, no. 23) is extremely unreactive compared to the less substituted parent 4-nitrocyclohexene itself (no. 21); stereochemistry, undetermined, is also important here.<sup>92a</sup>

The rate of proton removal from C<sub>3</sub>-C<sub>8</sub> nitrocycloalkanes (in 1:1 dioxane-water at 0°) has been studied<sup>120</sup>. Nitrocyclopropane does not react, whereas nitrocyclobutane reacts fastest; the reaction rate order is: C<sub>4</sub> > C<sub>5</sub> > C<sub>7</sub> > C<sub>8</sub> > C<sub>6</sub> ≫ C<sub>3</sub>. The order may be explained in terms of relative ring strain and steric repulsions of ring hydrogens in the reactant.

The stereochemistry of proton removal has been examined for substituted nitrocyclohexanes<sup>92a</sup>. The *cis* isomers react more rapidly than the *trans*. This effect is large in 2-arylnitrocyclohexanes in which the *cis* isomers react ca. 200 times faster. The rate enhancement effect has been ascribed in part to a relief of strain in the transition state proceeding from the axial nitro in the *cis*-isomers<sup>92a</sup>. There appears also to be a slight steric preference for abstraction of an equatorial hydrogen.

The stereochemistry of proton removal has been examined for nitrobicycloheptanes, -heptenes, -octanes, and -octenes (Table 3, nos. 17-20)<sup>120</sup>. Proton removal is fastest for the *endo* isomers, where attack occurs at the least hindered *exo* hydrogen. The rate acceleration for the *endo* isomers relative to *exo* is greatest for the most rigid bicycloheptene compound (26-fold). In the less rigid bicyclooctene series (no. 19) both isomers react at essentially the same rate which is nearly that observed with nitrobicyclooctane (no. 20).

Proton removal from nitroalkanes is catalyzed by acids<sup>37, 50, 51, 133, 140</sup>. This process resembles the acid-catalyzed enolization of aldehydes and ketones. The mechanism probably involves a protonated intermediate which is attacked by solvent or other base to produce a



nitronic acid directly (equations 14, 15)<sup>51,140a</sup>. For acid-catalyzed halogenations of nitroalkanes the rate is independent of the halogen employed, or halogen concentration, and is first order in nitro compound<sup>37</sup>. The proton removal step (equation 15) is slow compared to the oxygen protonation equilibrium (equation 14) and reaction of nitronic acid to form products (equation 16). The proton removal step is quite slow compared to the base-catalyzed process. Its rate is close to the auto-dissociation rate in water (Table 2). Table 4 summarizes the rate data obtained in *N* hydrochloric acid solution.

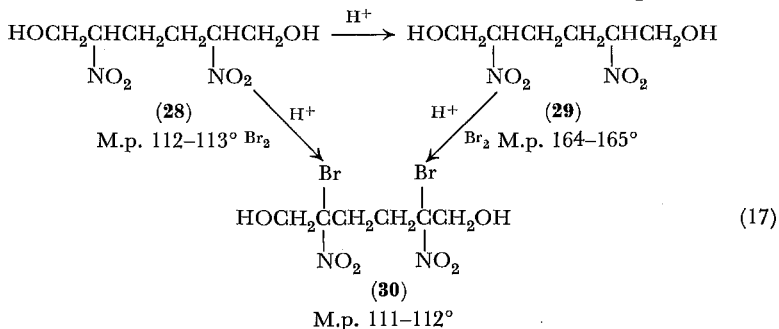
TABLE 4. Rates of acid-catalyzed reactions of nitro compounds in *N* hydrochloric acid<sup>51</sup>

Compound	Reaction	Temp. (°C)	Pseudo first order rate constant min <sup>-1</sup> × 10 <sup>5</sup>
Nitromethane	Bromination <sup>37</sup>	60	14
2-Nitropropane	Bromination <sup>37</sup>	60	3.0
2,5-Dinitro-1,6-hexanediol ( <b>28</b> )	Isomerization <sup>51</sup>	60	20 <sup>a</sup>
2,5-Dinitro-1,6-hexanediol ( <b>28</b> )	Isomerization <sup>51</sup>	100	200 <sup>a</sup>
2-Nitrooctane	Hydrolysis <sup>50</sup>	100	1.2 <sup>b</sup>
Nitromethane	Bromination <sup>37</sup>	35	0.9
Bromonitromethane	Bromination <sup>37</sup>	35	240
Dibromonitromethane	Bromination <sup>37</sup>	35	12,000

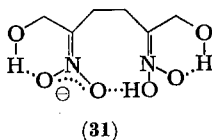
<sup>a</sup> Value corrected for reaction at one asymmetric center.

<sup>b</sup> Solvent "50%" ethanol, *N* hydrogen chloride.

Many reactions of nitroalkanes in acid solution require an initial acid-catalyzed proton removal to produce a nitronic acid. Examples are formation of carboxylic<sup>140a,141-143</sup> and hydroxamic acids<sup>153</sup> from primary nitroalkanes, and the acid-catalyzed Nef reaction<sup>52,142</sup>. The epimerization of low-melting 2,5-dinitro-1,6-hexanediol (**28**) to the high-melting form (**29**) is acid-catalyzed. The bromination of **28** and **29** to yield **30** is acid-, as well as base-catalyzed (equation 17).



Epimerization does not occur at a measurable rate in acid solution with the bisphenylurethane or bismethyl ether derivatives of **28**; the corresponding derivatives of **29** are not formed under conditions whereby **28**  $\rightarrow$  **29**. The epimerization **28**  $\rightarrow$  **29** does *not* occur at a measurable rate in pure water in the absence of added acid or basic catalysts. No formaldehyde is produced during the epimerization. A similar epimerization reaction is observed with the next higher homolog, 2,7-dinitro-1,7-heptanediol<sup>51</sup>. The epimerization is believed to be favored over the competing Nef reaction due to stabilization of the nitronate anion (e.g. **31**) by hydrogen bonding which slows hydrolysis, and a relatively rapid C-protonation rate<sup>52</sup>.



#### D. Ionization Constants of Nitronic Acids and Nitroalkanes

The ionization constants of nitronic acids may be expressed as


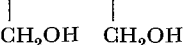
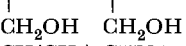
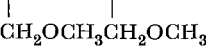
$$K_a^{Aci} = \frac{[H^+][A^-]}{[Aci]}$$

where  $[Aci]$  = the concentration of the nitronic acid and  $[A^-]$  is the concentration of nitronate anion<sup>57,59</sup>. Fewer values of  $K_a^{Aci}$  have been determined than  $K_a^{Nitro}$ . A complication in measurement lies in tautomerization to the more weakly acidic nitro form; but, by extrapolation of measurements back to zero time this error may be eliminated. Methods of determination include conductivity measurements<sup>28</sup>, polarography<sup>55</sup>, and potentiometric titrations<sup>59</sup>. Known values of  $K_a^{Aci}$  and  $K_a^{Nitro}$  are summarized in Table 5. Most nitronic acids are much stronger acids than the parent nitroalkanes (usually  $pK_a^{Nitro} - pK_a^{Aci} = 2-5$ ). However, this ratio narrows as acidity increases as shown in Figure 5. For very strong acids having  $pK_a \leq 0$ , such as nitroform,  $HC(NO_2)_3$ ,  $pK_a^{Aci} \cong pK_a^{Nitro}$ .

Substitution affects acidity of nitronic acids in the manner observed in carboxylic acids<sup>152</sup>.

There is evidence for intramolecular hydrogen bonding in 1,3-propanebisnitronic acid (**32**) and 1,4-butanebisnitronic acid<sup>52</sup>. A large  $K_a^I/K_a^{II}$  ratio is observed, similar to the values found for *cis*-caronic and dipropylmalonic acids (**33** and **34** respectively). For the

TABLE 5. Ionization constants of nitronic acids and nitroalkanes in water at 25°.

Nitroalkane	$\hat{p}K_a^{Acid^a}$	$pK_a^{Nitro^a}$	Ref.
A. Mononitroalkanes			
$CH_3NO_2$	3.25	10.21	47, 56, 59, 60, 113, 130, 132
$CH_3CH_2NO_2$	4.4	8.5	28, 31, 47, 52, 56, 59, 60, 114, 130, 132
$CH_3CH_2CH_2NO_2$	4.6	8.98	40, 59, 60, 115
$(CH_3)_2CHNO_2$	5.1	7.68	47, 59, 60, 116
$CH_3(CH_2)_3NO_2$	—	10	116
$CH_3CH_2CH(CH_3)NO_2$	—	9.4	116
 $NO_2$	6.35	8.3	109, 128
$C_6H_5CH_2NO_2$	3.9	6.8	34, 36, 38, 39, 53, 55, 64
$CH_3(CH_2)_5CH(CH_3)NO_2$	(5.3) <sup>b</sup>	(10) <sup>b</sup>	50, 52, 116
B. $\alpha,\omega$ -Dinitroalkanes			
$(O_2N)_2CHCH_2CH(NO_2)_2$	—	I 1.11 (20°) II 4.96 (20°)	115, 117
$O_2N(CH_2)_3NO_2$	I (1.95) <sup>b</sup> II 8.40	—	52
$O_2N(CH_2)_4NO_2$	I (3.30) <sup>b</sup> II 8.30	—	52
$O_2N(CH_2)_5NO_2$	I 3.46 II 7.57	—	52
$O_2N(CH_2)_6NO_2$	I 3.55 II 4.80	(10) <sup>b</sup>	52
$O_2NCH(CH_2)_2CHNO_2$	I (3.15) <sup>b</sup>	—	52
	II 9.17	—	52
$O_2NCH(CH_2)_3CHNO_2$	I 4.30	—	52
	II 8.45	—	52
$O_2NCH(CH_2)_2CHNO_2$	I (3.60) <sup>b</sup>	—	52
	II 8.35	—	52
C. 1,1-Dinitroalkanes			
$BrCH(NO_2)_2$	—	3.47	144
$ClCH(NO_2)_2$	—	3.80	144
$FCH(NO_2)_2$	—	7.70 (20°)	118, 145
$CH(NO_2)_3$	—	0.06 0.17 (20°)	56, 115, 144, 146-148
$NCCH(NO_2)_2$	—	-6.23	144

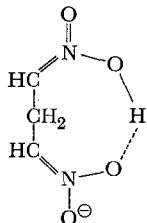
(continued)

TABLE 5—continued

Nitroalkane	$pK_a^{Acid^a}$	$pK_a^{Nitro^a}$	Ref.
C. 1,1-Dinitroalkanes			
$CH_2(NO_2)_2$	1.86	3.57	32, 56, 115, 117, 118, 145, 146, 148, 148a
$CH_3CH(NO_2)_2$	4.0	5.13	113–115, 144, 146, 148a 148–150
$CH_3CH_2CH(NO_2)_2$	4.1	5.6	114, 115, 148, 148a, 150
$HOCH_2CH_2CH(NO_2)_2$	—	4.44	156
$CH_3C(NO_2)_2CH_2CH(NO_2)_2$	—	1.36 (20°)	115, 117
$CH_3(CH_2)_2CH(NO_2)_2$	—	5.20	115, 148, 148a, 150
$(CH_3)_2CHCH(NO_2)_2$	—	6.75	148a 150,
$CH_3(CH_2)_3CH(NO_2)_2$	—	5.4	115, 148, 148a, 150, 151
$CH_3(CH_2)_4CH(NO_2)_2$	—	5.42 (20°)	115, 148a, 150, 151
$CH_3(CH_2)_8CH(NO_2)_2$	—	5.48 (20°)	115, 148a, 150, 151
$C_6H_5CH(NO_2)_2$	—	3.71	148a
D. $\alpha$ -Substituted Mononitroalkanes			
$Cl_2CHNO_2$	—	5.99	118
$F_2CHNO_2$	—	12.4	149
$ClFCHNO_2$	—	10.14	118
$BrCH_2NO_2$	—	8.2 (21°)	47
$ClCH_2NO_2$	—	7.20	47, 118
$CF_3CHFNO_2$	—	9.1	149
$CF_3CH_2NO_2$	—	7.4	149
$CH_3CHBrNO_2$	—	7.3 (21°)	47
$CH_3CHClNO_2$	—	6.8 (21°)	47
$H_2NCOCHClNO_2$	—	3.50	118
$H_2NCOCHFNO_2$	—	5.89	118
$H_2NCOCH_2NO_2$	—	5.18	118
$CH_3COCH_2NO_2$	—	5.1	56
$C_2H_5O_2CCHClNO_2$	—	4.16	118
$C_2H_5O_2CCHFNO_2$	—	6.28	118
$C_2H_5O_2CCH_2NO_2$	—	5.75	56, 113, 118
$C_2H_5O_2CCH(CH_3)NO_2$	—	7.4	113, 116
$C_2H_5O_2CCH(C_2H_5)NO_2$	—	7.6	116
$C_2H_5O_2CCH(i-C_3H_7)NO_2$	—	9.0	116
$C_6H_5COCH_2NO_2$	2.2	—	32
$C_2H_5O_2CCH(n-C_5H_{11})NO_2$	—	7.7	116
$C_2H_5O_2CH(C_6H_5)NO_2$	—	6.9	116

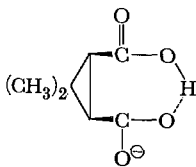
<sup>a</sup> Average of values reported at 25°, neglecting divergent values.<sup>b</sup> Estimated values.

longer chain 1,6-hexanebisnitronic acid  $K_a^I/K_a^{II} = 17.7$ , indicating



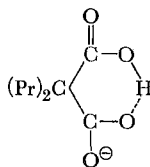
(32)

$$K_a^I/K_a^{II} = 2.9 \times 10^6$$



(33)

$$9.3 \times 10^5$$



(34)

$$2.8 \times 10^5$$

no intramolecular hydrogen bonding in the mononitronate anion.

The ionization constants of nitroalkanes may be expressed as

$$K_a^{\text{Nitro}} = \frac{[H^+][A^-]}{[\text{Nitro}]}$$

where  $[\text{Nitro}]$  = the concentration of the nitroalkane and  $[A^-]$  is the concentration of nitronate anion. A complication lies in the fact that the nitronate anion is in equilibrium with the more strongly acidic nitronic acid. One observes an apparent ionization constant,  $K_a^{\text{App}}$ , defined as

$$K_a^{\text{App.}} = \frac{[H^+][A^-]}{[\text{Nitro}] + [Aci]} \cong K_a^{\text{Nitro}}$$

where  $[Aci]$  = the concentration of nitric acid<sup>30,132</sup>. If  $K_a^{Aci}$  is known  $K_a^{\text{Nitro}}$  can be calculated from  $K_a^{\text{App.}}$ . For most nitroalkanes in solution the concentration of undissociated nitronic acid is very small and the  $[Aci]$  term may be neglected. Thus  $K_a^{\text{App.}}$  is very nearly equal to  $K_a^{\text{Nitro}}$ . Values of  $pK_a^{\text{Nitro}}$  are summarized in Table 5; most are determined conductometrically or spectrophotometrically, some by titration. Ionization constants of nitroalkanes are solvent dependent<sup>153</sup>.

Mononitroalkanes are relatively strong *pseudo* acids,  $pK_a^{\text{Nitro}} = 7-10$ . They are stronger than most monocarbonyl compounds (acetone  $pK_a = 20^{154}$ ), but are comparable to 1,3-diketones (acetylacetone  $pK_a = 9^{155}$ ). Nitromethane appears to be the weakest acid ( $pK_a^{\text{Nitro}} 10.2$ ).

Electron-withdrawing groups such as halogen (Cl, Br) and nitro are inductively acid-strengthening<sup>156</sup>. However, *alpha*-fluorine substitution is decidedly acid-weakening. This unusual effect has been attributed to stabilizing no-bond resonance in the nitroalkane<sup>118</sup>.

	$\text{ClCH}_2\text{NO}_2$	$\text{Cl}_2\text{CHNO}_2$	$\text{ClFCHNO}_2$
$pK_a^{\text{Nitro}}$	7.20	5.99	10.14



Electron-releasing alkyl groups, it appears, can also be acid-strengthening when  $\alpha$ -substitution occurs (on the carbon bearing the nitro group) in mononitroalkanes. Compare 1- and 2-nitropropane (**35**, **36**). Two factors may contribute to this effect which is

	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	$(\text{CH}_3)_2\text{CHNO}_2$
	( <b>35</b> )	( <b>36</b> )
$\text{p}K_{\text{a}}^{\text{Nitro}}$	8.98	7.68

associated with a relatively slower C-protonation rate of the nitronate ion derived from **36**. One is a stabilization of the nitronate anion by hyperconjugation<sup>157</sup>. Another may be a steric effect related to poor solvation about the nitronate carbon. On the other hand,  $\beta$ -alkyl substitution is acid-weakening (1-nitrobutane,  $\text{p}K_{\text{a}}^{\text{Nitro}}$  10), the expected result of electron-releasing bulky alkyl substitution.

In 1,1-dinitroalkanes and  $\alpha$ -nitroesters both  $\alpha$ - and  $\beta$ -alkyl substitution are acid-weakening (this effect is also observed in the carboxylic acids<sup>152</sup>). Dinitromethane ( $\text{p}K_{\text{a}}^{\text{Nitro}}$  3.57) is the strongest acid of the 1,1-dinitroalkane series. The 1,1-dinitro-*n*-alkanes ( $\text{C}_2$ – $\text{C}_9$ ) all have similar, but smaller, ionization constants ( $\text{p}K_{\text{a}}^{\text{Nitro}}$  5.2–5.7). An interesting compound is 1,1-dinitro-2-methylpropane (**38**). The weaker acidity of this more hindered  $\beta$ -alkyl substituted compound is probably associated with a relatively slower rate of proton removal (compare the unbranched isomer 1,1-dinitrobutane **37**). The  $\alpha$ -alkyl- $\alpha$ -nitroester  $\text{C}_2\text{H}_5\text{O}_2\text{CCH}(\text{CH}_3)\text{NO}_2$ ,  $\text{p}K_{\text{a}}^{\text{Nitro}}$  7.4,

	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{NO}_2)_2$	$(\text{CH}_3)_2\text{CHCH}(\text{NO}_2)_2$
	( <b>37</b> )	( <b>38</b> )
$\text{p}K_{\text{a}}^{\text{Nitro}}$	5.20	7.75

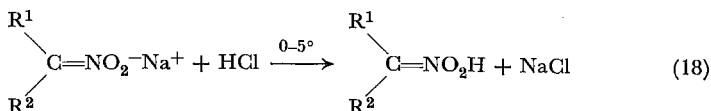
is weaker than the unbranched homolog  $\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2\text{NO}_2$ ,  $\text{p}K_{\text{a}}^{\text{Nitro}}$  5.75<sup>56,113,116,118</sup>. More rate data are needed to supplement the available  $\text{p}K_{\text{a}}$  measurements. A quantitative correlation of structure with  $\text{p}K_{\text{a}}^{\text{Nitro}}$  has been reported<sup>158</sup>.

### III. NITRONIC ACIDS

#### A. Preparation of Nitronic Acids

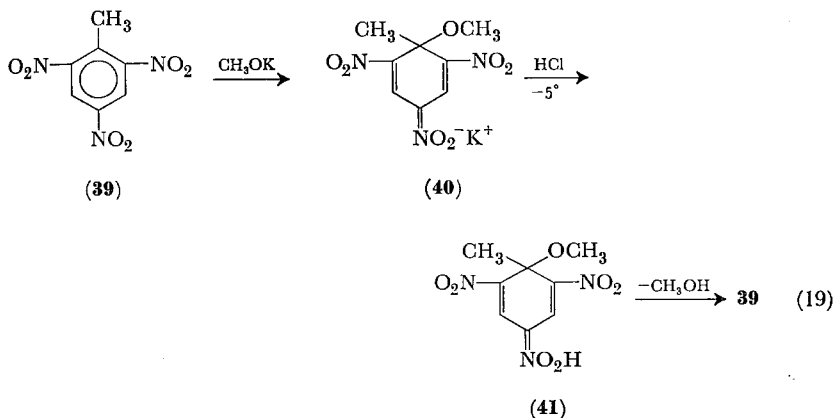
Several methods are available for preparation of nitronic acids. All depend on oxygen-protonation of a nitronate anion as the final step. Certainly the most convenient and frequently employed method is acidification of a nitronate salt (equation 18). The procedure often

involves preparation of a sodium or potassium salt by neutralization



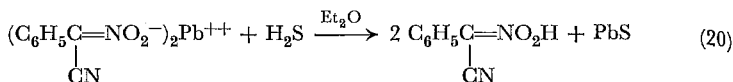
of a nitroalkane with aqueous alkali at 0–25°. Acidification of the salt usually proceeds best with an excess of a strong mineral acid, such as hydrochloric, keeping the temperature at 0–5°<sup>1,13</sup>. A low temperature is required to minimize Nef and other decomposition reactions. Use of a weak acid (acetic or carbonic) is preferred for C-protonation to regenerate a nitroalkane from its nitronate salt<sup>13,159,160</sup>. The weak acid permits a slightly acidic buffered solution having a relatively high concentration of nitronate ion needed for C-protonation to the nitroalkane. An excess of a strong mineral acid results in a strongly acidic solution having a low concentration of nitronate ion which inhibits C-protonation to the nitroalkane.

An interesting example of nitronic acid preparation is found in the acidification of a Meisenheimer-type salt<sup>161–168</sup>. Trinitrotoluene (**39**) reacts with potassium methoxide to form the thermodynamically stable potassium salt **40**<sup>161,169</sup>. Acidification of this salt with hydrogen chloride at –5° is reported to produce nitronic acid **41**,

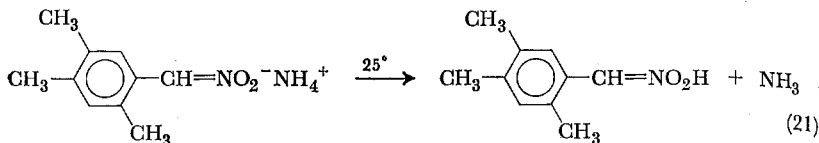


described as a dark red solid which explodes on heating<sup>170</sup> (equation 19). Many examples are known of reactions to form adducts like **40**<sup>168,171–174</sup>. Usually upon acidification of these substances a nitroaromatic compound is produced immediately since the nitronic acid decomposes so rapidly (**41** → **39**)<sup>73,171–175</sup>.

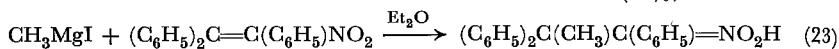
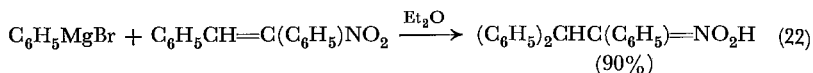
Salts other than those of the alkali metals have been employed for preparing nitronic acids. Reaction of lead  $\alpha$ -cyanophenylmethanenitronate with hydrogen sulfide produced the nitronic acid<sup>176</sup> (equation 20). Ammonium salts of nitronic acids on standing



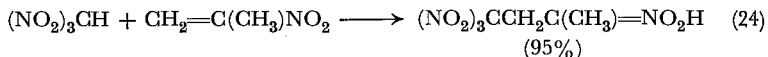
may evolve ammonia and produce a nitronic acid<sup>177</sup> (equation 21).



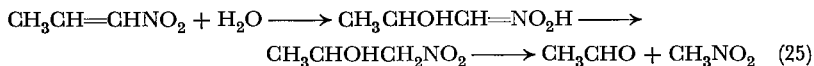
Another important general method for preparation of nitronic acids involves addition of anions to nitroolefins. Alkyl and aryl Grignard reagents add to  $\alpha$ -nitrostilbenes to form hindered nitronic acids in high yield<sup>65</sup> (equations 22 and 23). Addition of nitroform to



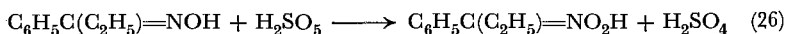
nitroolefins is a similar reaction and provides excellent yields of nitronic acids<sup>178</sup> (equation 24). Hydration of nitroolefins may involve



intermediate nitronate ion and nitronic acid formation, but retrograde Henry condensation or nitroalcohol formation is apparently favored at equilibrium<sup>179,179a</sup> (equation 25).



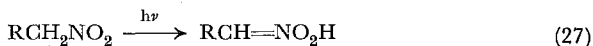
Oxidation of oximes appears to be a most useful route to nitronic acids. The method has not been fully developed, however. Oxidation of acetophenone and propiophenone oximes by Caro's acid (peroxymonosulfuric acid) leads to nitronic acids (not isolated) at room temperature<sup>83,180</sup> (equation 26). On warming, these nitronic acids rapidly tautomerize to the nitro form<sup>83</sup>. The use of other oxidizing



agents, including dinitrogen tetroxide<sup>83,181,182</sup>, manganese dioxide in acetic acid<sup>183</sup>, peroxytrifluoroacetic acid<sup>184</sup>, and nitric acid<sup>184a</sup>, for

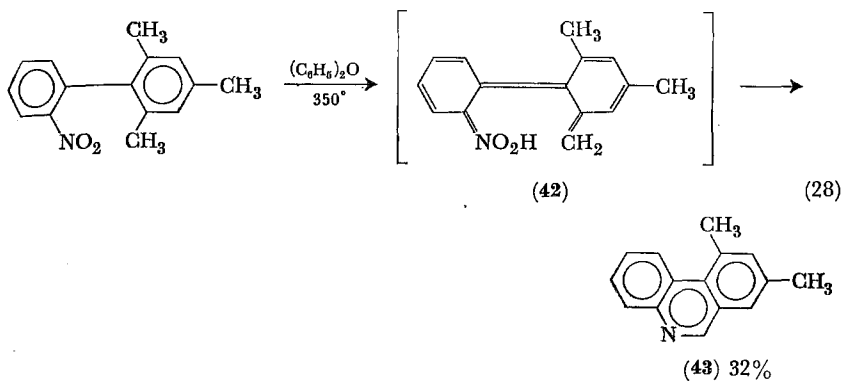
conversion of oximes to nitroalkanes, probably proceeds through a nitronic acid intermediate. Action of powerful oxidizing agents (peroxytrifluoroacetic acid) on hindered oximes should yield nitronic acids directly.

Photochemical conversion of nitroalkanes to nitronic acids is the subject of a recent patent<sup>185</sup> (equation 27). The reaction has been

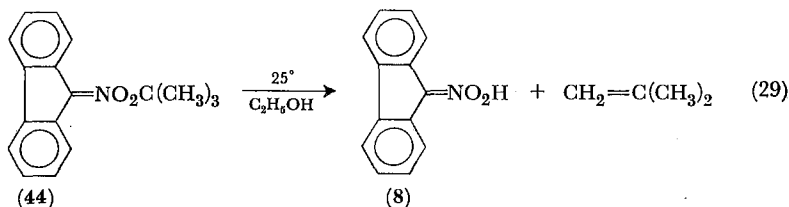


studied extensively with a limited group of compounds, the pyridyl-nitrophenylmethanes; nitronic acids derived from these compounds are unstable and tautomerize very rapidly to the nitro form (see section II.B)<sup>73,186</sup>. The scope of photochemical generation of nitronic acids has yet to be determined.

Thermal generation of a nitronic acid intermediate **42** has been postulated in the conversion of an *o*-nitrobiphenyl into the phenanthridine **43**<sup>187,188</sup> (equation 28).

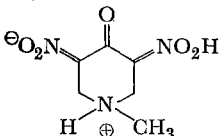
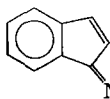


A nitronic ester has been converted into a nitronic acid. Potassium fluorene-9-nitronate and *t*-butyl bromide form *t*-butyl ester **44** in ethanol solution<sup>84</sup>. Ester **44** decomposes on standing at room temperature to form fluorene-9-nitronic acid (**8**) and butylene (equation 29). Application of this reaction to sodium phenylmethane-



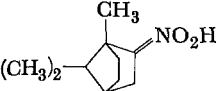
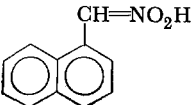
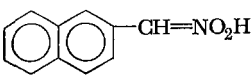
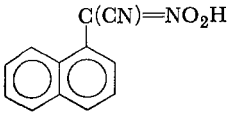
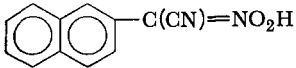
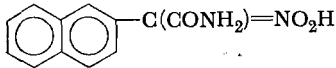
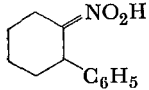
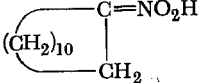
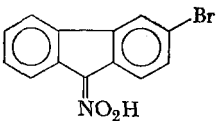
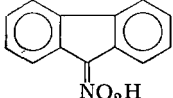
nitronate, however, led to phenylnitromethane rather than the nitronic acid<sup>84</sup>. Hydrolysis of nitronic esters under mild conditions

TABLE 6. Properties of nitronic acids.

Nitronic acid	M.p. (°C)	Half-life (approx.) at 25° <sup>a</sup>	Ref.
$(\text{O}_2\text{N})_2\text{C}=\text{NO}_2\text{H}$	50	few min	146, 190
$\text{CH}_3\text{CH}=\text{NO}_2\text{H}$	liquid	few min	32
$(\text{O}_2\text{N})_3\text{CCH}_2\text{C}(\text{CH}_3)=\text{NO}_2\text{H}$	91-91.5	2-3 h	178
$(\text{NC})_2\text{C}=\text{CHCH}=\text{NO}_2\text{H}$	liquid	few h	191
$(\text{O}_2\text{N})_3\text{CCH}_2\text{C}(\text{C}_2\text{H}_5)=\text{NO}_2\text{H}$	70.5-71	2-3 h	178
	119	few days	192
$(\text{O}_2\text{N})_3\text{CCH}_2\text{C}(n\text{-C}_3\text{H}_7)=\text{NO}_2\text{H}$	85-85.5	2-3 h	178
$(\text{O}_2\text{N})_3\text{CCH}_2\text{C}(i\text{-C}_3\text{H}_7)=\text{NO}_2\text{H}$	93-93.5	2-3 h	178
$2\text{-BrC}_6\text{H}_4\text{CH}=\text{NO}_2\text{H}$	100	several h	193
$4\text{-BrC}_6\text{H}_4\text{CH}=\text{NO}_2\text{H}$	89-90	12 h	33
$4\text{-ClC}_6\text{H}_4\text{CH}=\text{NO}_2\text{H}$	64	2 days	62
$4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}=\text{NO}_2\text{H}$	91	1 day	32, 194
$\text{C}_6\text{H}_5\text{CH}=\text{NO}_2\text{H}$	84	few days	1
$\text{C}_2\text{H}_5\text{O}_2\text{CC}(\text{CN})=\text{CHCH}=\text{NO}_2\text{H}$	liquid	several h	191
$(\text{CH}_3\text{O}_2\text{C})_2\text{C}=\text{CHCH}=\text{NO}_2\text{H}$	liquid	several h	191
$(i\text{-C}_3\text{H}_7)_2\text{C}=\text{NO}_2\text{H}$	69-70	1 day	195
$2\text{-BrC}_6\text{H}_4\text{C}(\text{CN})=\text{NO}_2\text{H}$	51-52	1 week	193
$4\text{-BrC}_6\text{H}_4\text{C}(\text{CN})=\text{NO}_2\text{H}$	64	1 day	196
$\text{C}_6\text{H}_5\text{C}(\text{CN})=\text{NO}_2\text{H}$	39-40	few h	176, 197, 198
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{NO}_2\text{H}$	45	few min	13, 83, 180
$4\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{NO}_2\text{H}$	65-70	few h	199
	50	few h	86
$2\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{CN})=\text{NO}_2\text{H}$	—	few h	200
$3\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{CN})=\text{NO}_2\text{H}$	—	few h	200
$4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{CN})=\text{NO}_2\text{H}$	—	few h	200
$3,5\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CH}=\text{NO}_2\text{H}$	63	few min	13, 159
$\text{C}_6\text{H}_5\text{C}(\text{C}_2\text{H}_5)=\text{NO}_2\text{H}$	—	few min	13, 83
$(\text{C}_2\text{H}_5\text{O}_2\text{C})_2\text{C}=\text{CHCH}=\text{NO}_2\text{H}$	b.p. 130- 140/0.2 mm <sup>b</sup>	few days	191
$\text{C}_6\text{H}_5\text{C}(\text{CO}_2\text{C}_2\text{H}_5)=\text{NO}_2\text{H}$	liquid	few days	197
$2,4,5\text{-(CH}_3)_3\text{C}_6\text{H}_2\text{CH}=\text{NO}_2\text{H}$	102-110	few h	177
$\text{C}_6\text{H}_5\text{C}(i\text{-C}_3\text{H}_7)=\text{NO}_2\text{H}$	54	few h	13

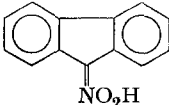
(continued)

TABLE 6—continued

Nitronic acid	M.p. (°C)	Half-life (approx.) at 25°a	Ref.
 <chem>CC1=C(C(=O)O[N+](=O)[O-])C=CC2=CC=CC=C12</chem>	74; 83	few min	201, 202
 <chem>C1=CC=C2C(=C1)C(=C(C=C2)C(=O)O[N+](=O)[O-])C3=CC=CC=C3</chem>	—	few h	200
 <chem>C1=CC=C2C(=C1)C(=C(C=C2)C(=O)O[N+](=O)[O-])C3=CC=CC=C3</chem>	—	few h	200
2,3,4,5-(CH <sub>3</sub> ) <sub>4</sub> C <sub>6</sub> HCH=NO <sub>2</sub> H	—	few h	177
 <chem>C1=CC=C2C(=C1)C(=C(C=C2)C(=O)O[N+](=O)[O-])C3=CC=CC=C3</chem>	—	few h	200
 <chem>C1=CC=C2C(=C1)C(=C(C=C2)C(=O)O[N+](=O)[O-])C3=CC=CC=C3</chem>	—	few h	200
 <chem>C1=CC=C2C(=C1)C(=C(C=C2)C(=O)O[N+](=O)[O-])C3=CC=CC=C3</chem>	155–156	several h	200
 <chem>C1=CC=C(C=C1)C(=C(C(=O)O[N+](=O)[O-])C2=CC=CC=C2)C3=CCCCC3</chem>	84–86	1 day	92
 <chem>C1=CC=C(C=C1)C(=C(C(=O)O[N+](=O)[O-])C2=CCCCCCCCC2)C3=CCCCC3</chem>	85–86	several days	203
 <chem>C1=CC=C2C(=C1)C(=C(C=C2)C(=O)O[N+](=O)[O-])C3=CC=CC=C3</chem>	132	several weeks	204
 <chem>C1=CC=C2C(=C1)C(=C(C=C2)C(=O)O[N+](=O)[O-])C3=CC=CC=C3</chem>	145–150; 132–135	several weeks	84, 85
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NO <sub>2</sub> H	90	few h	33
2-ClC <sub>6</sub> H <sub>4</sub> (4-BrC <sub>6</sub> H <sub>4</sub> )CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	101–118	>6 months	27

(continued)

TABLE 6—continued

Nitronic acid	M.p. (°C)	Half-life (approx.) at 25°C <sup>a</sup>	Ref.
4-ClC <sub>6</sub> H <sub>4</sub> (4-BrC <sub>6</sub> H <sub>4</sub> )CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	48–65	4–20 h	27
2-ClC <sub>6</sub> H <sub>4</sub> (4-IC <sub>6</sub> H <sub>4</sub> )CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	116–130	>6 months	27
2-ClC <sub>6</sub> H <sub>4</sub> (4-ClC <sub>6</sub> H <sub>4</sub> )CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	75–80	>6 months	27
(2-ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	42–55	4–20 h	27
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	70–77	4–20 h	27
2-ClC <sub>6</sub> H <sub>4</sub> (4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	89–94	8 days	27
4-ClC <sub>6</sub> H <sub>4</sub> [2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]CHC(CH <sub>3</sub> )=NO <sub>2</sub> H	47–70	4–20 h	27
	80–84	several weeks	205

<sup>a</sup> Approximate time for undiluted sample to liquefy or exhibit evident decomposition.

<sup>b</sup> About 90% of the sample is reported to decompose during the distillation.

may be expected to yield products other than nitronic acids (section IV.C.1). Thus, the conversion of nitronic esters to nitronic acids appears to be a reaction of limited scope and utility, particularly since most esters are prepared from nitronate salts.

Fluorene-9-nitronic acid (8) may also be prepared by reduction of 9-bromo or 9-iodo-9-nitrofluorene with potassium iodide<sup>84</sup>. This reaction should be considered unique, however, since reduction of other 1-bromo-1-nitroalkanes with mild reducing agents produces nitroalkanes<sup>189</sup>.

Table 6 lists most of the known, isolable nitronic acids in order of molecular formula. Usually only solids are sufficiently stable to be isolated in pure form. Melting points and approximate half-lives are given where this information is available. The approximate half-life (measured at room temperature) is arbitrarily chosen as the time required for liquefaction or evident decomposition of a compound. Since no standardized procedure has been employed for this measurement, the times listed are necessarily very approximate. The information should prove useful, however, in correlating structure with stability.

## B. Physical Properties of Nitronic Acids

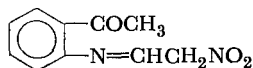
Ionization constants of nitronic acids are summarized in Table 5, melting points in Table 6.

The ultraviolet spectra of nitronic acids resemble closely the spectra of nitronate anions (salts) and nitronic esters<sup>206</sup>. A strong  $\pi - \pi^*$  band ( $\epsilon \cong 10000$ ) is found near 220–230  $m\mu$  for simple aliphatic nitronic acids measured in ethanol or water<sup>47,52</sup>. The corresponding nitronate anions absorb at nearly the same wavelength (usually ca. 10  $m\mu$  higher, depending on structure) with approximately equal extinction coefficients<sup>47,52,207,208</sup>. Absorption spectra of nitronate anions have been published elsewhere<sup>120,209,210</sup>. Olefinic or aromatic ring conjugation produces the expected bathochromic shift in absorption maximum wave length [ $C_6H_5CH=NO_2$   $\lambda_{max}^{H_2O}$  284  $m\mu$  ( $\epsilon$  20000);  $C_6H_5CH=NO_2-Na$   $\lambda_{max}^{H_2O}$  294  $m\mu$  ( $\epsilon$  25000)]<sup>53,211–214</sup>. The nitronic acids produced by irradiation of pyridyl and phenylnitrophenylmethanes are highly colored with strong absorption bands near 580–700  $m\mu$  (see section II.B)<sup>74,75</sup>; in this group of compounds the corresponding nitronate salts absorb at wave lengths ca. 10  $m\mu$  lower (ethanol solvent)<sup>75</sup>.

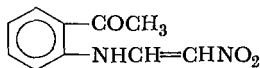
The infrared spectra of nitronic acids are characterized by  $C=N$  absorption near 1620–1680  $cm^{-1}$ <sup>150,178,206</sup>. This absorption is in the region of oxime  $C=N$  absorption, 1640–1684  $cm^{-1}$ <sup>215</sup>. Conjugation shifts the absorption to slightly lower frequencies; fluorene-9-nitronic acid absorbs at 1652  $cm^{-1}$ <sup>211</sup>. Nitronic esters absorb intensely in the region 1610–1660  $cm^{-1}$  ( $C=N$ ). Nitronate salts absorb at much lower frequencies, as one observes with carboxylate salts<sup>215</sup>. Sodium alkanenitronate salts reveal a  $C=N$  band in the region 1587–1605  $cm^{-1}$ <sup>216</sup>.

The infrared absorption of nitronic acids in the OH stretching region resembles that of carboxylic acids. A free OH stretching band is absent<sup>211</sup>. One observes the broad absorption band envelope in the region 2500–3000  $cm^{-1}$  characteristic of associated weak acids<sup>206,211</sup>.

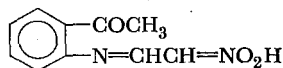
Few nmr spectra of nitronic acids have been reported<sup>217–219</sup>. From nmr, infrared, and ultraviolet spectra measurements it was concluded that the imine **45a** exists as the nitronic acid **45c**, rather than nitroolefin **45b**, in methanol or deuteriochloroform; in the latter solvent an AB quartet was observed at  $\tau$  2.38, 3.27<sup>217</sup>.



(45a)  
M.p. 124–125°



(45b)



(45c)  
 $\lambda_{max}^{CH_3OH}$  388  $m\mu$  ( $\epsilon$  23694)

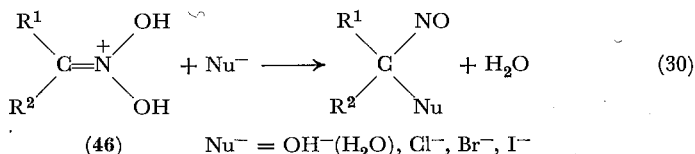


### C. Reactions of Nitronic Acids

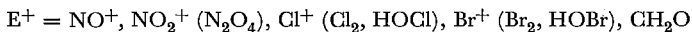
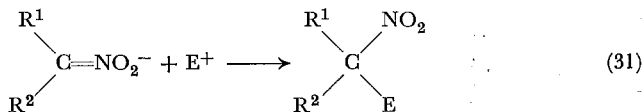
Nitronic acids are quite reactive. The C=N bond undergoes many addition reactions. Nitronic acids are also good oxidizing agents and are readily reduced to oximes. They participate in autooxidation-reduction reactions. The reactions which are discussed in this section are principally those of nitronic acids and nitronate anions in *acid* solution. Reactions of nitronate salts, or of nitronate ions in basic solution, with a few exceptions, are not discussed. Formation of nitronic esters and anhydrides is described in following sections.

#### I. Addition reactions of nitronic acids

Two distinct patterns of addition are evident: (a) In acid solution a protonated nitronic acid (46) adds nucleophiles such as halide and hydroxide ion; simultaneously the nitronic group ultimately

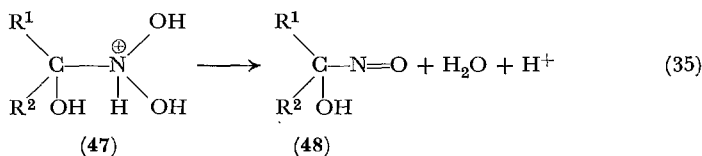
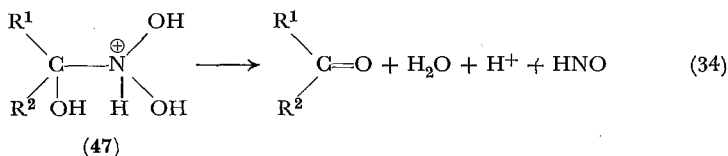
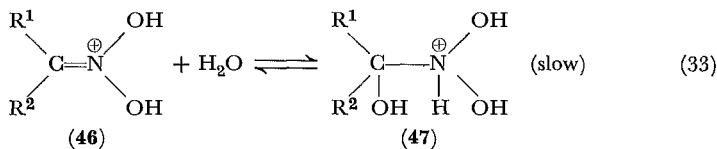
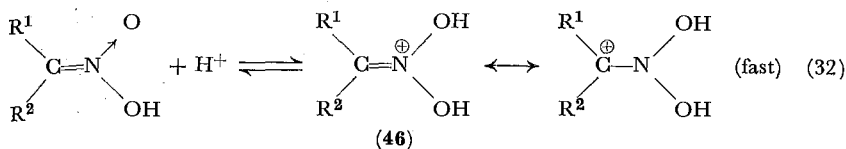


becomes nitroso in the product (equation 30). Alternatively, in strongly acidic solution a dehydration to a nitrile oxide may precede addition of water to form a hydroxamic acid. (b) Nitronate anions exist in acid solution, although they are present in much lower concentration than in basic solution. They undergo addition with electrophiles such as nitrosonium, and nitronium ions, halogens, and hypohalogen acids. The nitronate group becomes nitro in the product (equation 31).



*a. Nucleophilic addition.* Nucleophilic additions occur on a protonated nitronic acid. Addition of water to nitronic acids is one of the most important nucleophilic addition reactions. It is a useful route to aldehydes and ketones (Nef reaction), hydroxamic acids, and carboxylic acids.

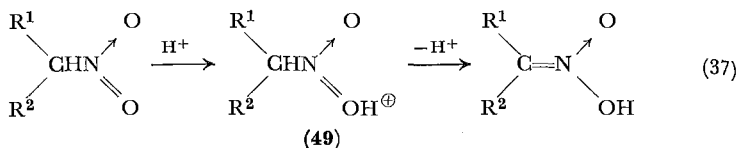
The Nef reaction<sup>15</sup> is important synthetically. It has been reviewed<sup>4,220</sup> and its mechanism studied<sup>46,47,209,221-226</sup>. The reaction involves treatment of a nitronate salt or nitronic acid with aqueous acid; in effect, it is the acid-catalyzed hydrolysis of a nitronic acid. The mechanism may be expressed by the equations 32, 33, 34, and 35<sup>209,222,227</sup>. The details of the decomposition of the hydrated



intermediate **47** are not completely understood. The formation of the blue color which frequently accompanies the Nef reaction may be explained by formation of the hydroxynitroso compound **48**<sup>209</sup>. The initially formed nitrogenous product of the reaction is believed to be the unstable intermediate nitroxyl (HNO) which forms nitrous oxide (equation 36).



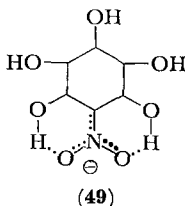
A direct acid-catalyzed Nef reaction is possible without starting with a nitronate salt or a nitronic acid<sup>50,51,141,228</sup>. 2-Octanone has been obtained directly from *d*-2-nitrooctane by refluxing with aqueous hydrochloric acid<sup>50</sup>. The recovered nitro compound retained all its optical activity indicating, in this example, that the Nef reaction was faster than tautomerization of the intermediate nitronic acid, formed by an acid-catalyzed process (equation 37).



Studies have been made to determine optimum conditions for securing high yields of aldehydes and ketones in the Nef reaction<sup>46,47,105,223</sup>. The reaction is pH dependent. A low pH (0.1–1) favors Nef reaction over tautomerization which occurs more readily at pH 3–5 (see Table 7)<sup>47</sup>. A very low pH (as with 85% sulfuric acid) favors hydroxamic acid formation, possibly proceeding by a different mechanism<sup>222</sup>.

The yields of aldehydes and ketones on Nef hydrolysis vary (0–100%) and depend on the structure of the nitronic acid (Table 8), as well as on pH (Table 7). Tautomerization to the parent nitro compound is an important competing reaction, although other reactions can occur<sup>65,240</sup>. Simple, unsubstituted aliphatic nitronic acids readily undergo the Nef reaction<sup>32,160</sup>. However, branching near the nitronate carbon, which hinders attack, decreases yields<sup>221,229,231,232</sup>. Compounds of structure  $\text{Ar}_3\text{CCH}(\text{Ar})\text{NO}_2$  fail to undergo the Nef reaction<sup>65</sup>.

Factors which stabilize nitronate anions (and nitronic acids) inhibit the Nef reaction<sup>32</sup>. These include resonance stabilization, presence of electron-withdrawing groups, and hydrogen bonding. *p*-Nitrophenylnitromethane<sup>222</sup> and 1,1,1,2,2,3,3-heptafluoro-5-nitropentane<sup>233</sup> fail to undergo the Nef reaction. Nitrodesoxyinsitols fail to undergo the Nef reaction<sup>237,238</sup> and may be recovered unchanged; stabilization of the nitronate anion by hydrogen bonding **49** has been suggested to explain this result<sup>51</sup>. Homoallylic resonance in the



nitronic acid of 5-nitronorbornene (Table 8, no. 20) has been suggested as an explanation for failure of the Nef reaction<sup>240,241</sup>; however, the nitro compound is not recovered<sup>240</sup>.

Ring strain in the transition state leading to a product having an exocyclic double bond is probably the explanation for failure of the

TABLE 7. Products of nitronic acid decomposition in water at various pH.  
(0.1 M solutions of nitronic acid in buffer solutions at 21°)<sup>47</sup>

A. Ethanenitronic acid

pH	$C_2H_5NO_2$	$CH_3CHO$	$CH_3CH=NOH$	$CH_3C \begin{array}{l} \nearrow NO_2 \\ \searrow NOH \end{array}$	$NO_2^-$
3.4	100	0	0	0	0
2.9	85	7	3	4	0
2.07	59	28	6	6	0
1.50	27	61	6	6	0
1.18	6	82	6	5	0
0.45	0	98	0	0	0

B. Propane-2-nitronic acid

pH	$(CH_3)_2CHNO_2$	$(CH_3)_2CO$	$(CH_3)_2C=NOH$	$(CH_3)_2C \begin{array}{l} \nearrow NO \\ \searrow NO_2 \end{array}$	$NO_2^-$
5.4	100	0	0	0	0
5	85	7-8	7-8	0	7-8
4.25	44	20	19	15	4
3.75	27	26	25	20	5
3.10	10	30	30	29	0
2.5	3	32	31	32	0
2.2	0	33	32	33	0
2	0	39	32	29	0
1.5	0	49	28	22	0
1.15	0	80	12	7	0
0.50	0	100	0	0	0

C. Cyclohexanenitronic acid

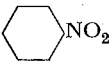
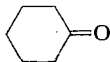
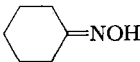
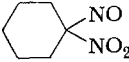

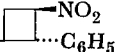


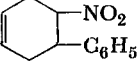
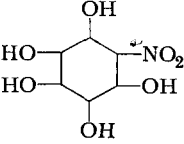
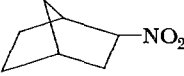
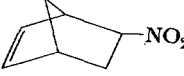
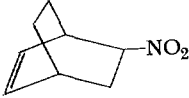
pH					$NO_2^-$
4.8	100	0	0	0	0
4.15	43	20	21	14	7
3.05	6	32	31	31	0
2.40	0	38	31	30	0
1.50	0	70	24	5	0
1	0	84	15	1	0
0.15	0	100	0	0	0

TABLE 8. Syntheses and attempted syntheses of carbonyl compounds by the Nef reaction.

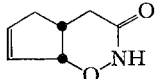
No.	Nitroalkane	Yield carbonyl compound (%)	Ref.
1.	$\text{CH}_3\text{NO}_2$	100	47
2.	$\text{CH}_3\text{CH}_2\text{NO}_2$	77	47, 229
3.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	80	47, 229
4.	$(\text{CH}_3)_2\text{CHNO}_2$	84	47, 229
5.	$\text{CH}_3(\text{CH}_2)_3\text{NO}_2$	85	229
6.	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NO}_2$	82	229
7.	$(\text{CH}_3)_2\text{CHCH}_2\text{NO}_2$	32	229
8.	$(\text{CH}_3)_3\text{CCH}_2\text{NO}_2$	very low	230, 231
9.	$(\text{CH}_3)_2\text{C}(\text{CH}_2\text{NO}_2)_2^a$	0	232
10.	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{NO}_2$	0	233
11.	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{OH})\text{NO}_2$	50	179
12.	$(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{CH}_2\text{NO}_2$	0	179
13.	 -NO <sub>2</sub>	56	209
14.	$(\text{C}_6\text{H}_5)_2$ - 	very low	234, 235
15.	 -NO <sub>2</sub>	89	209
16.	 -NO <sub>2</sub>	85-97	47, 209
17.		88	236
18.		0	237, 238
19.	 -NO <sub>2</sub>	80	226
20.	 -NO <sub>2</sub>	0 <sup>b</sup>	221, 226, 236, 239-241
21.	 -NO <sub>2</sub>	68	242

(continued)

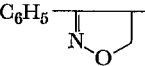
TABLE 8—continued

No.	Nitroalkane	Yield carbonyl compound (%)	Ref.
22.	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NO <sub>2</sub>	0	22
23.	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> )NO <sub>2</sub> <sup>c</sup>	94	65
24.	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>3</sub> )CH(C <sub>6</sub> H <sub>5</sub> )NO <sub>2</sub> <sup>c</sup>	0 <sup>d</sup>	65

<sup>a</sup> Monosodium salt employed.

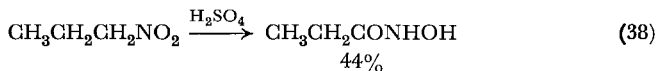
<sup>b</sup>  was obtained in 42% yield with 9.2% aqueous HCl at -20 to -10°<sup>240</sup>.

<sup>c</sup> Nitronic acids employed rather than salts.

<sup>d</sup>  (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> was obtained in 70% yield with methanolic hydrogen chloride.

Nef reaction with certain strained nitrocycloalkanes. This effect may explain the failure of 5-nitronorbornene to undergo Nef reaction in contrast to the behavior of 5-nitrobicyclo[2,2,2]-2-octene (Table 8, no. 21). An example of the effect of ring strain coupled with steric hindrance is shown by 1-nitro-2,3,3-triphenylcyclobutane (no. 14) which undergoes the Nef reaction in very low yield<sup>234,235</sup>. Nitrocyclobutane provides a lower yield (56%) of ketone than nitrocyclopentane (89%) and nitrocyclohexane (85–97%)<sup>47,209</sup>.

Reaction of concentrated sulfuric acid (85–100%) with salts of primary nitroalkanes leads to hydroxamic acids<sup>243–245</sup>. The subject has been reviewed<sup>246</sup> and the mechanism discussed<sup>222,240,247,248</sup>. Direct conversion of nitroalkanes to hydroxamic acids has been observed in concentrated sulfuric acid<sup>143,244</sup> (equation 38). Nitronic

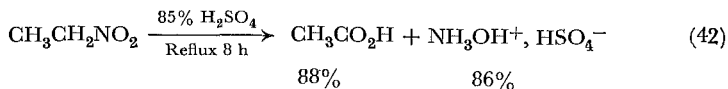


acid should be considered a primary reaction intermediate<sup>244,249,250</sup>. The nitronic acid would be protonated as in the first step of the Nef reaction. Two mechanisms may be considered<sup>222</sup>:

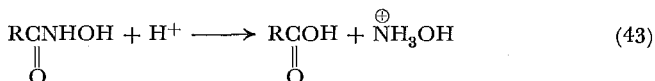
(1) *Nitrile oxide mechanism*<sup>240</sup>. In strong acid solution—in contrast to dilute aqueous acid used in the Nef reaction—dehydration of intermediate **46** might be expected to be favored over hydration. The resulting nitrile oxide intermediate **50** could rehydrate to



Reaction conditions for carboxylic acid formation are somewhat more vigorous than those required for hydroxamic acid formation. Solutions of nitroalkane in 85 % sulfuric acid, or concentrated hydrochloric acid-acetic acid, are heated under reflux for several hours (equation 42). Yields of both acid and hydroxylamine are often

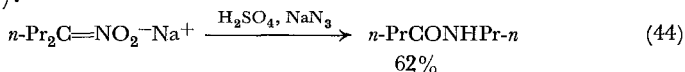


high (80–90 %) <sup>143</sup>. Hydroxamic acids may be isolated when lower temperatures or shorter reaction times are employed <sup>143, 261</sup>. It seems reasonable that hydroxamic acids are intermediates in the reaction. Thus the mechanism would involve the steps for hydroxamic acid formation, followed by acid-catalyzed hydrolysis of the hydroxamic acid <sup>140a, 270</sup> (equation 43),

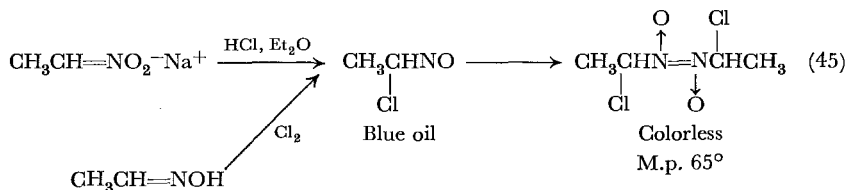


One commercially feasible hydroxylamine synthesis employs 1,2-dinitroethane which forms oxalic acid <sup>267–269</sup>. Another process employs nitromethane <sup>142, 255, 256, 258, 266, 271</sup>.

An extension of the reaction to secondary nitroalkanes permits preparation of amides by including azide as a reactant <sup>272, 273</sup> (equation 44).



Hydrogen halides add to nitronic acids <sup>105</sup>. With nitronate salts in ether solvent the blue  $\alpha$ -halonitroso product <sup>203, 249</sup> may occasionally be isolated as a colorless dimer <sup>189, 249, 274</sup> (equation 45). (The  $\alpha$ -

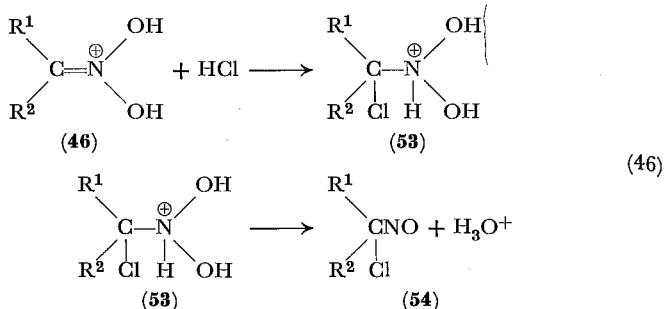


halonitroso compounds are also readily prepared by halogenation of oximes <sup>189, 274, 274a</sup>).

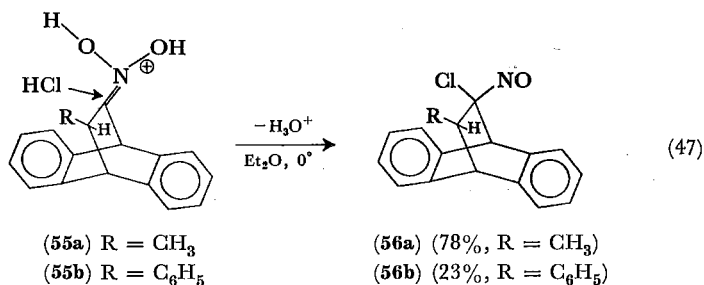
The reaction mechanism is believed to depart from the protonated nitronic acid intermediate **46** common to nucleophilic addition reactions of nitronic acids. Addition of hydrogen chloride to form



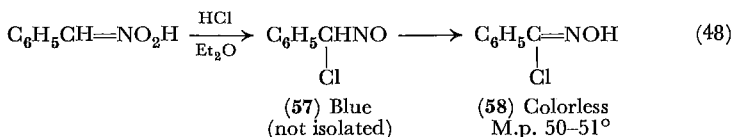
**53**, followed by dehydration, produces the nitroso product **54** (equation 46),



The stereochemistry of this addition has been examined (equation 47)<sup>105</sup>. The potassium salt of **55** was treated with hydrogen chloride in ether at 0°. The resulting nitroso group appears *trans* to the adjacent R group (phenyl, methyl) in product **56** in the kinetically controlled process. Interestingly, **56a** could not be prepared by chlorination of the required oxime<sup>105</sup>.

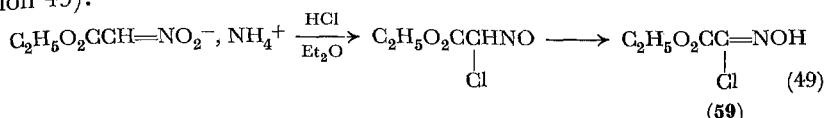


The  $\alpha$ -halonitroso compounds derived from primary nitronic acids tautomerize readily to form hydroxamic acid chlorides ( $\alpha$ -chlorooximes)<sup>248, 250, 274, 274a, 275</sup>. The blue phenylchloronitroso-methane **57** is observed in solution when phenylmethanenitronic



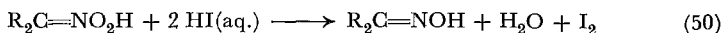
acid is treated with hydrogen chloride in ether; it has not been isolated, however, and rearranges to colorless benzohydroxamic acid chloride (**58**)<sup>249, 274, 275</sup> (equation 48). The ammonium salt of

ethyl nitroacetate forms ethyl chlorooximinacetate (59)<sup>250</sup> (equation 49).



Reaction of hydrogen bromide with nitronic acids to form  $\alpha$ -bromonitrosoalkanes appears not to have been reported. The less stable  $\alpha$ -bromonitrosoalkanes are prepared by bromination of oximes<sup>189, 274</sup>.

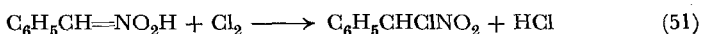
Hydrogen iodide (aqueous) reduces nitronic acids to oximes and is the basis for a quantitative analytical determination; the liberated iodine is titrated with sodium thiosulfate<sup>276</sup> (equation 50).



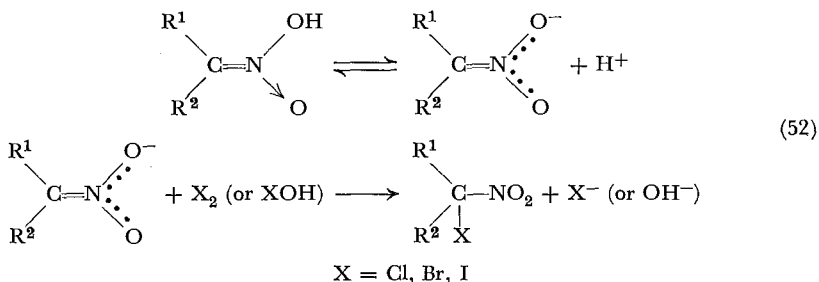
The  $\alpha$ -halonitrosoalkanes may be oxidized to  $\alpha$ -halonitroalkanes with peroxytrifluoroacetic acid<sup>189</sup>.

*b. Electrophilic addition.* Electrophilic additions to nitronic acids occur on the nitronate anion. The following discussion is limited to reactions of nitronic acids in acid solution. With a few exceptions the many reactions of nitronate salts and nitronate anions in basic solution—Michael addition and aldol-type condensations, for example—will be discussed in the second volume of this treatise.

Halogens, or hypohalogen acids, add readily to nitronic acids to yield  $\alpha$ -halonitroalkanes<sup>170, 201</sup> (equation 51). The mechanism

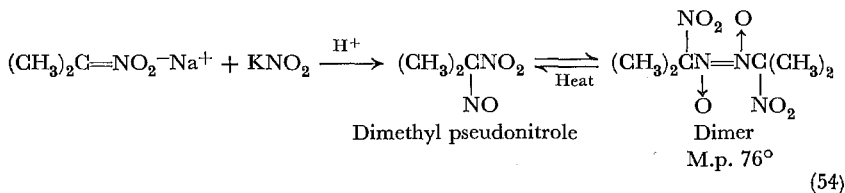
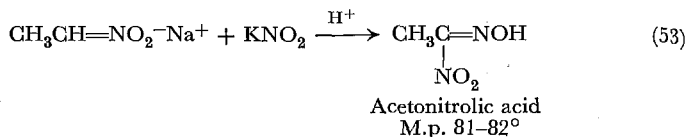


involves addition of halogen to a nitronate anion (equation 52).

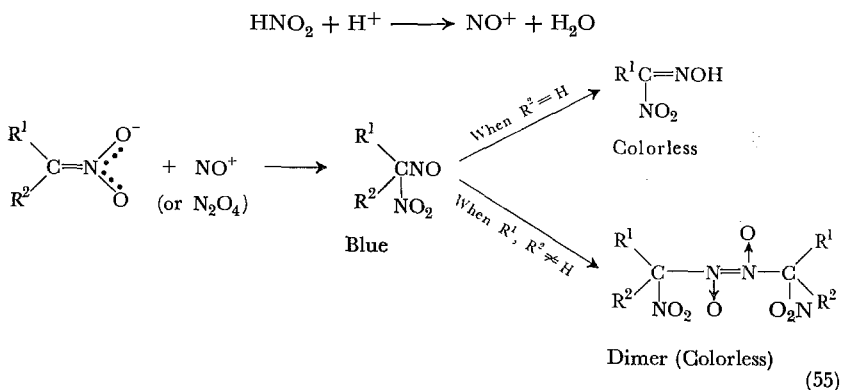


Addition of iodine monochloride (ICl) produces the iodo compound,  $\text{R}^1\text{R}^2\text{CINO}_2$ , and chloride ion<sup>209</sup>. It is to be noted that  $\alpha$ -halonitroalkanes are most conveniently prepared by halogenation of nitronate salts.

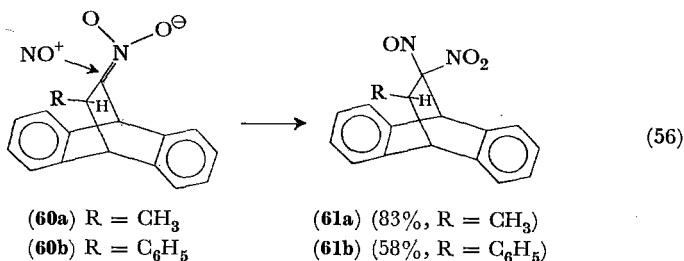
Reaction of nitrous acid with nitronic acids and salts yields pseudonitroles (blue)<sup>105,201,277-279</sup>. These pseudonitroles derived from primary nitronic acids isomerize very readily to nitrolic acids<sup>170,259,277-279</sup>. The reaction was discovered by Victor Meyer (1873)<sup>278,279</sup> who first prepared acetonitrolic acid and dimethyl pseudonitrole by addition of dilute acid to a mixture of nitroalkane salt and potassium nitrite (equations 53 and 54). The blue pseudonitroles may be isolated in the solid state or in solution; often they are isolated as colorless crystalline dimers. On melting, the dimers form blue liquids containing pseudonitrole monomer (equation 54).



The reaction mechanism for pseudonitrole formation very likely involves nitronate anion, rather than nitronic acid, in a reaction with nitrosonium ion ( $\text{NO}^+$ ) or  $\text{N}_2\text{O}_4$ <sup>105</sup> (equation 55).

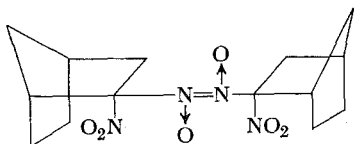


The stereochemistry of pseudonitrole formation has been examined in the system shown in equation 56<sup>105</sup>. Addition of  $\text{NO}^+$  to **60** occurs *cis* to the R group ( $\text{C}_6\text{H}_5$ ,  $\text{CH}_3$ ) leading to a *trans* arrangement of R



and nitro (product development control) in the product **61**; repulsion of R and incipient NO<sub>2</sub> in the transition state may account for the result.

Since nitrous acid may be formed from nitrite on acidification of nitronate salts (the nitrite formed *in situ* by air oxidation of nitronates<sup>280</sup> or autooxidation-reduction of nitronic acids<sup>47</sup>), pseudonitrole and nitrolic acid formation is a side reaction which often results on regeneration of nitroalkanes from their salts<sup>160, 180, 226, 249, 281-283</sup>. This reaction is favored by use of aged nitronate solutions at 0-25°, and by slow addition of the nitronate salt to the acid<sup>226, 283</sup>. For example, sodium bicyclo[2,2,1]heptane-2-nitronate when added slowly to aqueous hydrochloric acid at room temperature leads to a 20% yield of pseudonitrole dimer **62**<sup>226</sup>. Conditions have been developed for

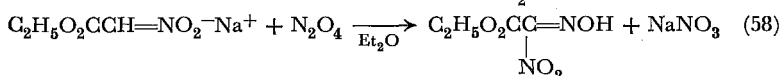
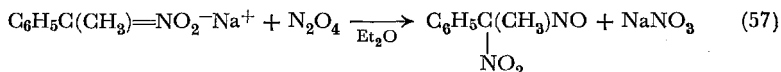


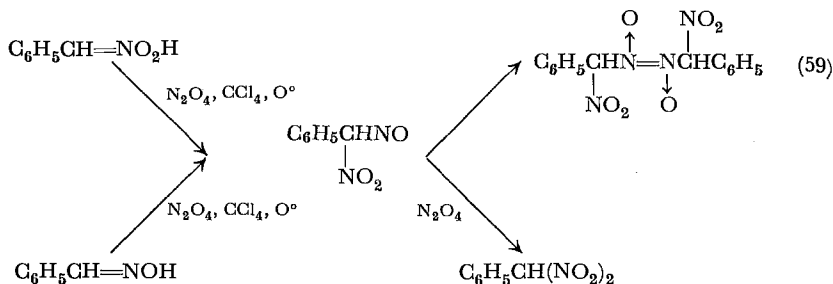
(62)

M.p. 108°

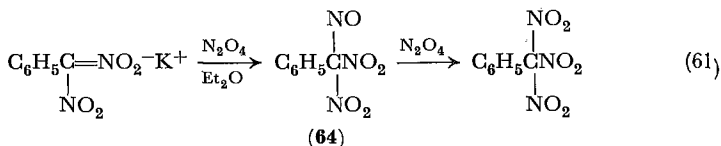
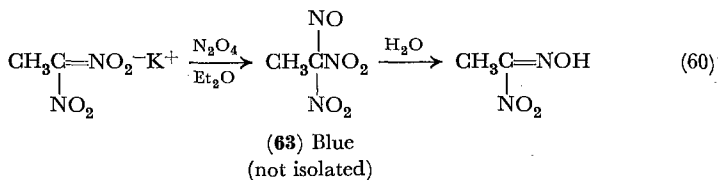
securing high yields of pseudonitroles by simple acidification of nitronate salts; the process has been patented<sup>281-283</sup>.

Addition of dinitrogen tetroxide to nitronic acids<sup>181, 182, 284</sup> or nitronate salts<sup>285, 286</sup> also leads to pseudonitroles or nitrolic acids, a reaction discovered by Bamberger<sup>83</sup>. Oximes also may be used as reactants<sup>83, 181, 182, 285</sup>. Excess N<sub>2</sub>O<sub>4</sub> converts phenylpseudonitrole into α,α-dinitrotoluene<sup>181, 182, 284</sup> (equations 57-59).



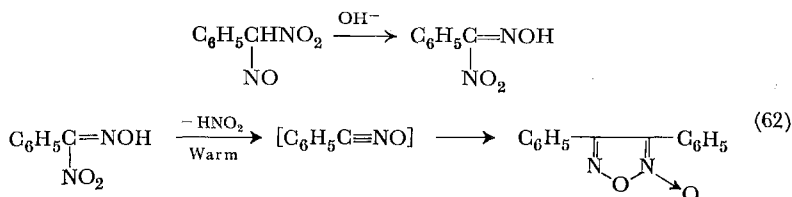


Attempts to convert 1,1-dinitroalkanes into 1,1-dinitro-1-nitrosoalkanes by this method have led to other products<sup>181</sup>. Potassium 1-nitroethanenitronate forms acetonitrolic acid, presumably due to hydrolysis by adventitious water of the observed blue intermediate, 1,1-dinitro-1-nitrosoethane (**63**)<sup>286</sup> (equation 60).  $\alpha$ -Nitrophenylmethanenitronate forms trinitromethylbenzene by oxidation of the intermediate nitroso compound **64**<sup>181,284</sup> (equation 61).

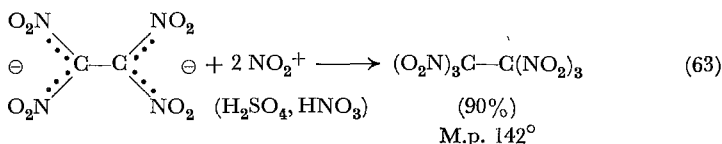


Pseudonitroles are quite reactive compounds and may become converted into other substances under the usual preparation conditions. The isomerization of primary pseudonitroles (those having an *alpha* hydrogen) to nitrolic acids occurs very readily in the aliphatic series. No simple aliphatic pseudonitrole of structure  $\text{RCH}(\text{NO})\text{NO}_2$  appears to have been described. Phenyl pseudonitrole,  $\text{C}_6\text{H}_5\text{CH}(\text{NO})\text{NO}_2$ , has been prepared and isolated as its dimer which was found to be unstable at room temperature, decomposing in one day, and melting with explosive decomposition<sup>181</sup>. With aqueous alkali it readily isomerizes to benzonitrolic acid<sup>181</sup>. Dimers derived from disubstituted pseudonitroles,  $\text{R}^1\text{R}^2\text{C}(\text{NO})\text{NO}_2$ , are stable<sup>279,282</sup>. Benzonitrolic acid decomposes on standing in nitrous acid solution, or on warming, to yield diphenylfuroxan

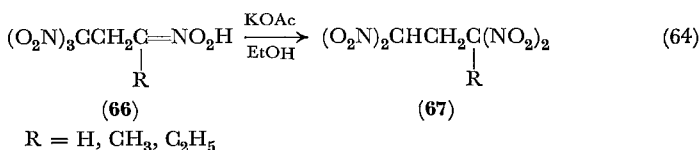
(65)<sup>277</sup>; benzonitrile oxide may be an intermediate (equation 62).



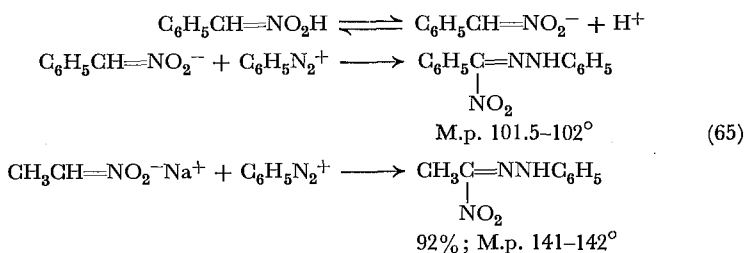
The nitration of dipotassium tetranitroethane with mixed acid (5–70°) to produce hexanitroethane in 90% yield should be considered an electrophilic addition of nitronium ion to a bisnitronate ion<sup>287</sup> (equation 63).



The conversion of the trinitromethyl substituted nitronic acid **66** into a bisdinitromethyl derivative **67** is an interesting rearrangement<sup>288,289</sup>. The reaction, carried out in ethanol with potassium acetate<sup>288</sup> or ammonium hydroxide<sup>289</sup>, may involve intramolecular or intermolecular nitration of the intermediate nitronate ion by the  $\omega$ -trinitromethyl group (equation 64).



Nitronic acids, nitronate salts, and certain nitroalkanes react with diazonium salts to form  $\alpha$ -nitroaldehyde hydrazones in high yield<sup>6,170,259,290–299</sup>. The reaction was discovered by Victor Meyer<sup>290,291</sup>. It involves an addition to a nitronate anion (equation 65). The

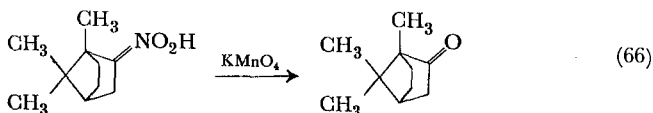


$\alpha$ -nitroaldehyde hydrazones react with diazomethane to produce orange-red methyl esters of phenylazonitronic acids (see section IV.A.1)<sup>6,295-299</sup>.

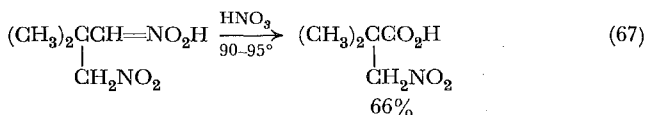
Phenyl isocyanate reacts with arylmethanenitronic acids to produce diphenylurea<sup>33</sup> and unidentified oils<sup>32,201</sup>.

## 2. Oxidation and reduction reactions

The reaction of nitronic acids with oxidizing agents has not been extensively studied. Bornane-2-nitronic acid is oxidized to camphor with permanganate<sup>201,230</sup> (equation 66). Oxidation of 2-(nitromethyl)-alkanenitronic acids (formed *in situ* from the sodium salts) occurs

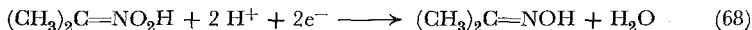


smoothly with nitric acid (but not sulfuric acid) to yield 2-nitromethyl-alkanoic acids<sup>232</sup> (equation 67). The hindered nitronic acid,



$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_6\text{H}_5)=\text{NO}_2\text{H}$ , was found to be inert to sodium peroxide or ozone<sup>65</sup>. The oxidation of secondary nitronate anions by oxygen in basic solution to yield ketones<sup>280</sup> is not observed in acid solution.

Reduction of nitronic acids to oximes occurs readily in excellent yields, with a wide variety of reducing agents (Table 9). The polarographic half-wave potential at pH 0 for reduction of propane-2-nitronic acid to acetoxime is  $-0.9$  v; at pH 2,  $E_{1/2} = 1.05$  v<sup>44</sup>



(equation 68). Reduction of cyclohexanenitronic acid to cyclohexanone oxime (70–80% yield) has been accomplished with several reducing agents (see Table 9 (equation 69)). Hydroxylamine reduces cyclododecanenitronic acid to the oxime in 91% yield<sup>203</sup>.

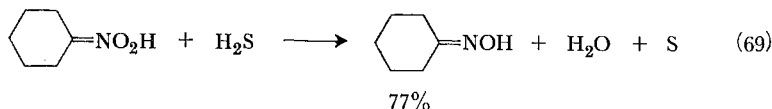
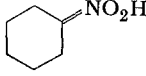
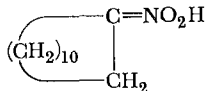


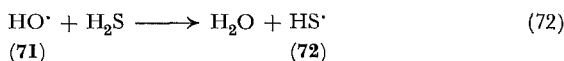
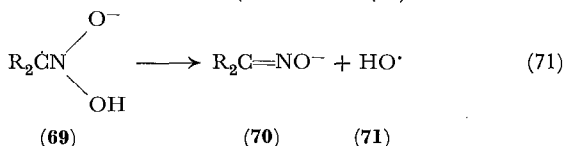
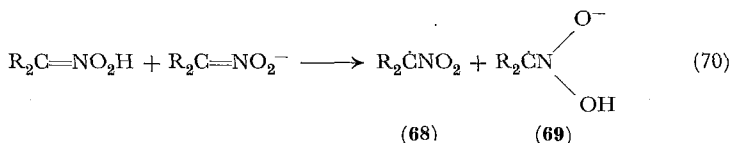
TABLE 9. Reduction of nitronic acids to oximes.

Nitronic acid	Reducing agent	Yield oxime (%)	Ref.
$\text{CH}_3\text{CH}=\text{NO}_2\text{H}$	HI	100 <sup>a</sup>	276
$\text{CH}_3\text{CH}_2\text{CH}=\text{NO}_2\text{H}$	HI	100 <sup>a</sup>	276
$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{H}$	HI	100 <sup>a</sup>	276
	HI	100 <sup>a</sup>	276
	$\text{H}_2\text{S}$	77	300, 301
	$\text{H}_2\text{S}_2\text{O}_3$	80	302
	$\text{NH}_2\text{OH}$	—	303
	$\text{NH}_4\text{Cl}$ , $\text{CH}_3\text{OH}$	70	304
$4\text{-BrC}_6\text{H}_4\text{CH}=\text{NO}_2\text{H}$	NaHg	—	33
$\text{C}_6\text{H}_5\text{CH}=\text{NO}_2\text{H}$	NaHg	—	33
	$\text{NH}_2\text{OH}$	91	203
$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_6\text{H}_5)=\text{NO}_2\text{H}$	$\text{AlHg}$	—	65

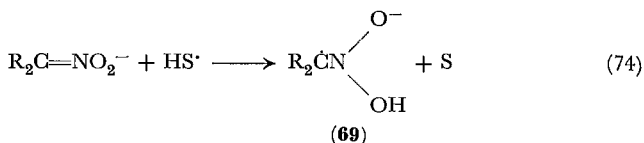
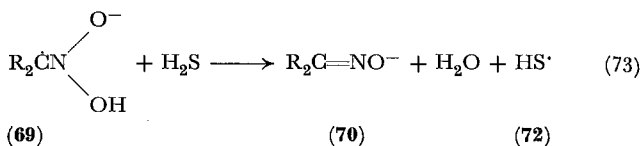
<sup>a</sup> Quantitative analytical method; product not isolated.

Phenylmethanenitronic acid is reduced to the oxime with zinc and alkali and sodium amalgam<sup>33</sup>; aluminum amalgam has also been used for nitronic acid reduction<sup>65</sup>. Complete reduction of a nitronic acid to the corresponding amine appears not to have been reported; catalytic (Pt) hydrogenation should effect it.

The mechanism of nitronic acid reduction may involve a radical-chain process initiated by electron transfer between nitronic acid and nitronate anion (equation 70)<sup>305</sup>. Reduction of the radical-anion intermediate **69** could include steps 71–74. These suggested steps include dissociation of **69** into oximate ion **70** and hydroxyl radical (**71**) (equation 71), followed by reduction of hydroxyl by hydrogen



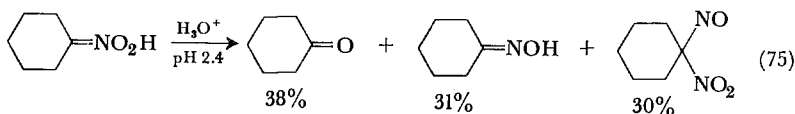




sulfide to hydrosulfide radical (72) (equation 72). Alternatively, a concerted reaction of 69 with hydrogen sulfide (equation 73) may be more likely to occur in the presence of the reducing agent. Finally, another electron exchange (equation 74) would regenerate 69 and continue the chain.

An interesting and complex reaction exhibited by nitronic acids is an autooxidation-reduction<sup>13,27,47,48,65,84,203,204,226,296,306,307</sup>. This process has been observed in solution and in the solid state. Oxime is a characteristic product. Other products are ketones, substituted 1,2-dinitroethanes, nitrolic acids, nitrous acid, and oxides of nitrogen.

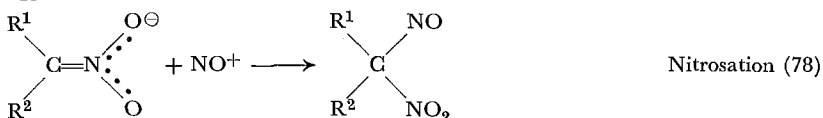
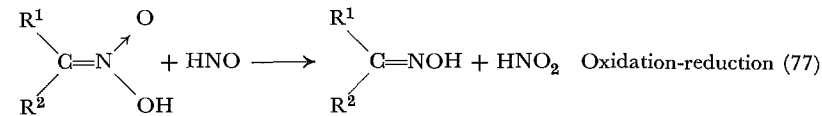
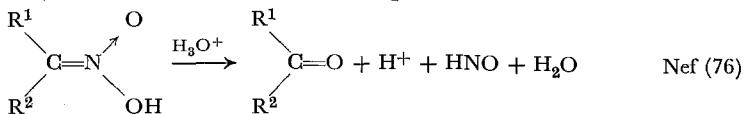
In solution the reaction is dependent on the structure of the nitronic acid and on the pH. It has been studied quantitatively in dilute aqueous solution by Armand<sup>47,48</sup> (Table 7, section III.C.1.a., summarizes some of the data). For example, cyclohexanenitronic acid at pH 2.4 produces the following products<sup>47</sup> (equation 75). Tautomerization to nitrocyclohexane is important only at higher pH.



At lower pH (<1) one obtains only the Nef product, cyclohexanone. It is to be noted that oxime is not a Nef product. The autooxidation-reduction reaction is catalyzed by acids. At certain acid concentrations (pH 2–4) it competes with tautomerization and Nef reaction. Secondary nitronic acids undergo the reaction much more readily than primary.

A mechanism for the reaction is suggested by the facts above. Nitronic acids are very easily reduced to oximes and are present in unprotonated form in rather high concentration at pH 2–4. The initial step(s) is the Nef hydrolysis (equation 76). The reducing agent

is believed to be the Nef hydrolysis product, nitroxyl, or its equivalent (equation 77); *cf.* the mechanism of oxime formation (equations 70–74). The stoichiometry of the process which indicates that

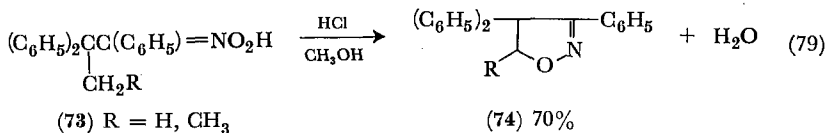


oxime and pseudonitrole form in equal amounts, and in yields always less than that of ketone, suggests an immediate reaction of nitrous acid with remaining nitronic acid (equation 78). A relatively slow tautomerization of nitronic acid to nitroalkane (observed with secondary nitronic acids) evidently favors the oxidation process.

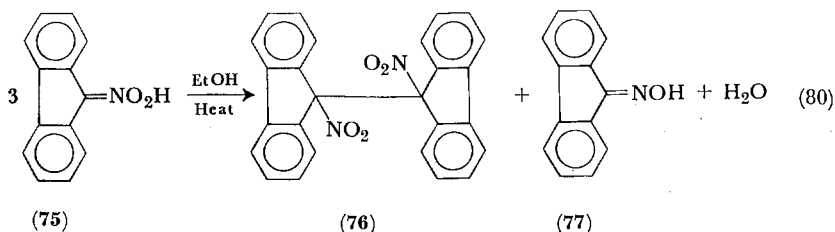
The conversion of nitronic acids into oximes by boiling in ethanol solvent<sup>84,203</sup> could involve decomposition of an ethyl nitronate (see section IV.C.2), as well as autooxidation-reduction.

Decomposition of nitronic acids occurs in the absence of solvents<sup>13, 27, 65, 296</sup>, but this process has received no systematic study. Bamberger<sup>296</sup> and Konowalow<sup>13</sup> observed the facile formation of benzophenone and its oxime from diphenylmethanenitronic acid. The decomposition, which is believed to include autooxidation-reduction, often leads to oxime, ketone, and oxides of nitrogen. Tautomerization also occurs. The decomposition is accelerated by traces of water. It is inhibited by accumulation of bulky groups about the nitronate carbon (see half-lives listed in Table 6, section III.A) which also inhibits Nef hydrolysis.

An interesting intramolecular oxidation-reduction is observed with the very hindered nitronic acid **73**, which does not tautomerize to nitroalkane nor undergo the Nef reaction. In methanolic hydrogen chloride **73** forms the 3,4,4-triphenyl-2-isoxazoline (**74**) by participation of the neighboring alkyl group, CH<sub>2</sub>R<sup>65</sup> (equation 79).

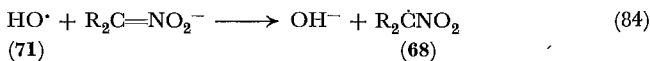
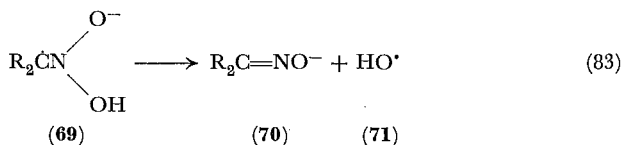
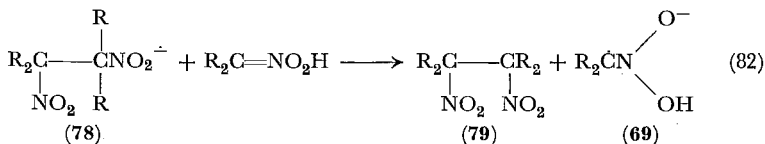
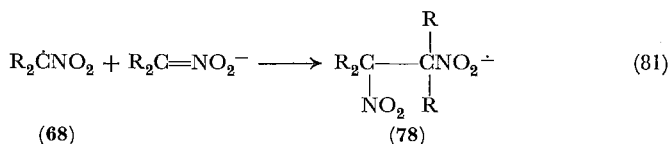


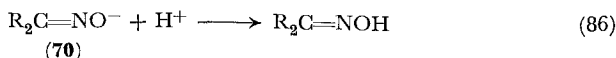
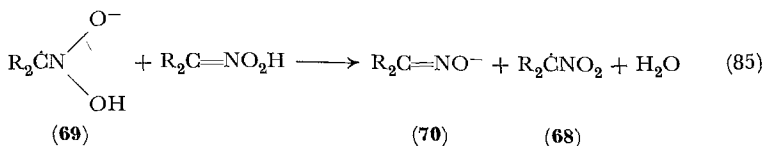
Bimolecular coupling products (1,2-dinitroethanes such as **76**) are obtained from fluorene-9-nitronic acid (**75**) and its ring-substituted derivatives by warming in ethanol<sup>[84, 205, 308–310]</sup>. Fluorenone oxime (**77**) is also formed in 26% yield<sup>84</sup> (equation 80). Although other nitronic acids have not been observed to undergo this reaction, nitronate salts can form bimolecular coupling products on oxidation<sup>311, 312</sup>. Dimer **76** is also prepared in quantitative yield



by reaction of the potassium salt of **75** with iodine<sup>313</sup>, or by heating 9-iodo-9-nitrofluorene<sup>314</sup>. It may also be prepared in 71% yield by electrolysis of the **75** salt<sup>313</sup>.

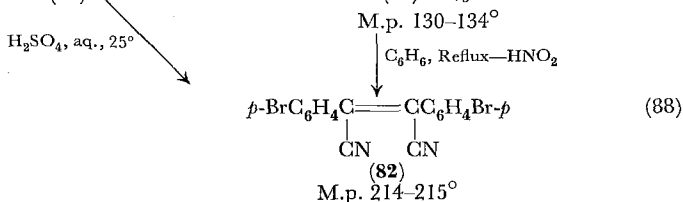
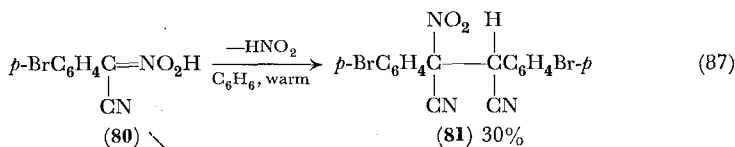
Formation of dimer **76** is believed to involve the spontaneously initiated process leading to radicals **68**, **69** (equation 70)<sup>305, 312, 314–316</sup>. The following equations (81–86) are suggested to explain dimerization





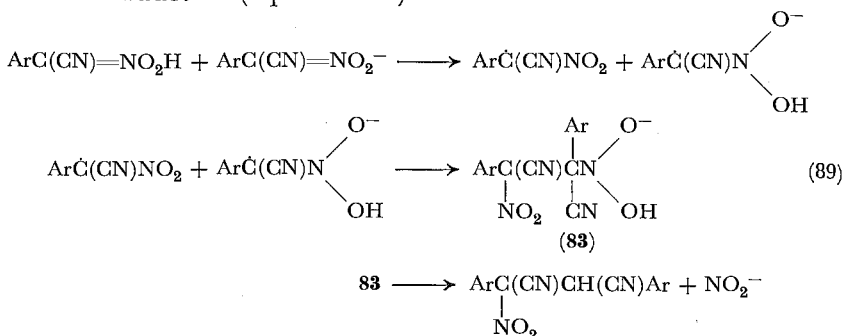
and oxime formation. Formation of a radical anion intermediate (78) (equation 81) would be favored over a reaction between radicals 68 and 69<sup>312,315</sup>. An exchange would lead to dimer 79 (equation 82). Oxime formation is explained by the sequence suggested for nitronic acid reduction (equation 83) involving dissociation of 69 into oximate ion 70 and hydroxyl radical 71. Radical 68 is regenerated by electron exchange between hydroxyl radical and nitronate ion (equation 84). Alternatively, a direct electron transfer between 69 and nitronic acid could lead to the same result (equation 85). Finally, protons made available by required ionization of the nitronic acid can produce oxime (equation 86).

The decomposition of *p*-bromophenylcyanomethanenitronic acid (80) into dimeric products, in the solid state or in benzene solution, may be a radical process<sup>196</sup>. Gentle heating leads to a 1-nitro-1,2-dicyano derivative 81 (equation 87); a 1,2-dinitroethane derivative was not isolated<sup>196</sup>. Prolonged heating or a slightly higher temperature leads to a 1,2-dicyanostilbene (82). *o*-Bromophenylcyanomethanenitronic acid behaves similarly<sup>193</sup>. In dilute aqueous sulfuric

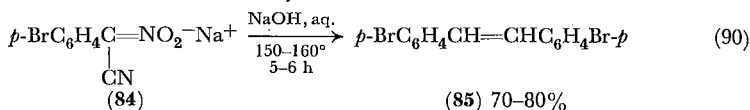


acid solution at room temperature 80 is converted quantitatively into the dicyanostilbene derivative 82<sup>196,197</sup> (equation 88). The mechanism may involve combination of spontaneously initiated

radical and radical anion, with loss of nitrite from the initially formed adduct **83** (equation 89).



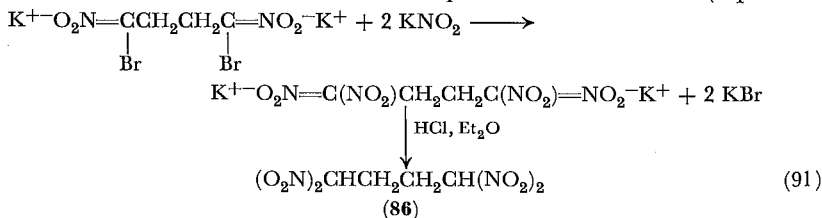
Heating strongly in aqueous alkali converts the nitronate salt **84** into an unsubstituted stilbene **85**<sup>196</sup> (equation 90). Certain other aryl nitronate salts behave similarly<sup>193,317</sup>.



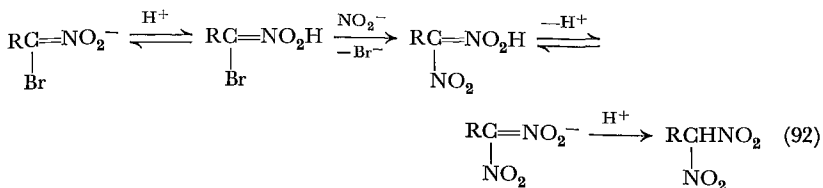
### 3. Reactions of $\alpha$ -halonitronic acids

The  $\alpha$ -halonitronic acids,  $\text{RC(X)=NO}_2\text{H}$  ( $\text{X}$  = halogen), are somewhat unique in the ease with which they undergo displacement of halide ion by various nucleophiles. Reactions of these substances are believed to occur with a nitronic acid, rather than a nitronate intermediate. Examples of such reactions include the ter Meer<sup>318</sup> hydrolysis to carboxylic acids<sup>319</sup>, and coupling to 1,2-dinitroethylenes<sup>313,320</sup>.  $\alpha$ -Halonitronic acids are reactive and attempts to isolate them have failed<sup>32</sup>. They are readily reduced to halide and nitronate anion<sup>321</sup>.

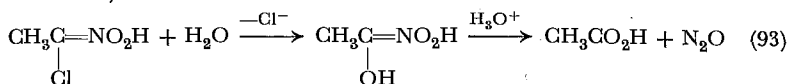
The ter Meer reaction<sup>318</sup> involves a displacement of halide by weakly nucleophilic nitrite ion<sup>322</sup>. For example, 1,1,4,4-tetranitrobutane (**86**) may be prepared by reaction of the dipotassium salt of 1,4-dibromo-1,4-dinitrobutane with potassium nitrite<sup>323</sup> (equation



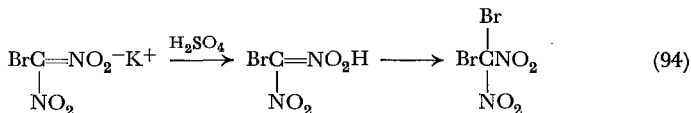
91). The mechanism is depicted as a displacement on the  $\alpha$ -halonitronic acid<sup>322</sup> (equation 92).



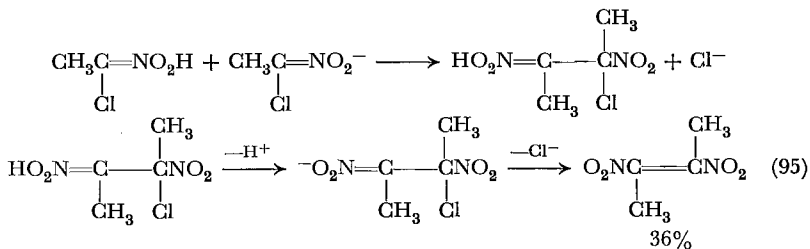
The mechanism of  $\alpha$ -chloronitroalkane hydrolysis has been studied<sup>319,324</sup>. The reaction is interpreted as a displacement of chloride, by water, from an  $\alpha$ -chloronitronic acid intermediate (equation 93).



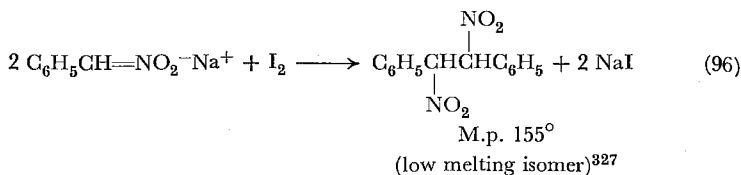
Halonitromethanenitronic acids are unstable<sup>32,325,326</sup>. They undergo a complex rearrangement to dihalodinitromethanes<sup>325</sup> (equation 94).



1,2-Dinitroethylene coupling products of  $\alpha$ -halonitronic acids apparently are formed by displacement of halide—by attack of nitronate anion on an  $\alpha$ -halonitronic acid<sup>320</sup>. For example, 1,2-dinitro-2-butene may be formed in 36% yield from 1-chloro-1-nitroethane by treatment with ca. one mole-equivalent of aqueous sodium hydroxide solution at 10–15° (pH ca. 9) (equation 95).



Coupling of  $\alpha$ -halonitroalkanes and nitronate salts can lead to 1,2-dinitroethanes<sup>84,310,313,327,328</sup> (equation 96). This reaction may be conducted *in situ* by treating nitronate salts with iodine<sup>84,310,313,327</sup>. Such reactions apparently involve nitronate ions rather than nitronic

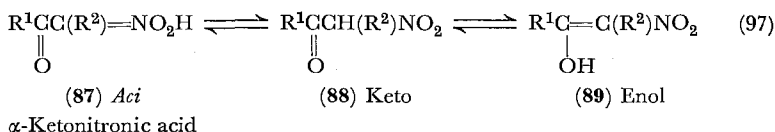


acids. They may proceed by displacement<sup>84</sup> or radical-anion<sup>84,314</sup> mechanisms.

#### 4. Reactions of ketonitronic acids

Several  $\alpha$ - and  $\gamma$ -ketonitronic acids have been described and their somewhat unique chemistry is discussed in this section. Ketonitronic acids are usually prepared by acidification of their alkali metal salts; the salts of  $\alpha$ -nitroketones are conveniently prepared by the alkaline nitration of ketones<sup>329,330</sup>.  $\alpha$ -Nitroketones may be prepared by reaction of  $\alpha$ -bromoketones with silver nitrite<sup>331</sup> or sodium nitrite<sup>332</sup>.

For all  $\alpha$ -ketonitronic acids there exist three possible tautomeric forms: *aci* or  $\alpha$ -ketonitronic acid (**87**), keto (**88**), and enol (**89**) (equation 97).



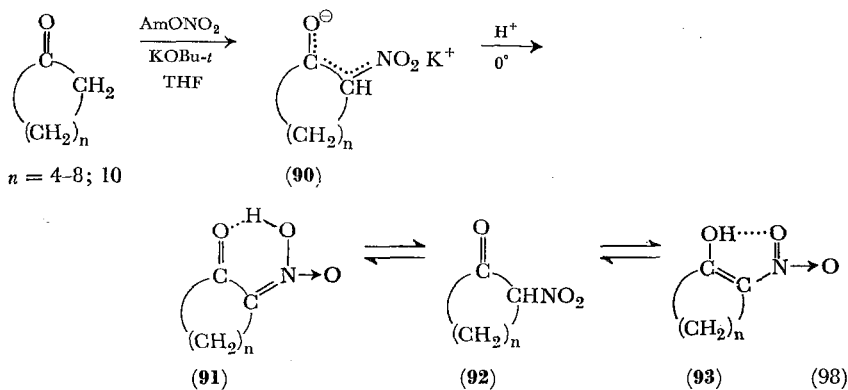
Compounds representing each of the three forms have been reported. In solution the three forms can exist in tautomeric equilibrium with the common anion,  $\text{R}^1\text{COC}(\text{R}^2)=\text{NO}_2^-$ . The interconversion is catalyzed by bases and acids.

The relative concentration of **87**, **88**, and **89** may be measured by ultraviolet, infrared, and nmr spectroscopy<sup>330,333,334</sup>, and with the aid of bromine titration<sup>36</sup>. A complication lies in the presence of the fourth species, the common anion, particularly in protic solvents. The composition of the equilibrium mixture is solvent dependent (Table 10)<sup>330</sup>. The keto form of  $\alpha$ -nitroketones (**88**) is favored in polar protic solvents such as ethanol as one observes with  $\beta$ -dicarbonyl compounds<sup>338</sup>. Enol form **89** is favored more in aprotic solvents such as carbon tetrachloride or hexane suggesting an intramolecularly hydrogen-bonded form<sup>330</sup>. Its concentration usually remains low, however.

The amount of  $\alpha$ -ketonitronic acid (**87**) present in these equilibria is believed to be quite small. However, freshly prepared solutions, obtained by acidification of salts of  $\alpha$ -ketonitronic acids, probably contain relatively high concentrations of nitronic acid form; on standing the nitroketone usually results<sup>329</sup>.

The acyclic  $\alpha$ -ketonitronic acids derived from  $\alpha$ -nitroacetophenone and  $\alpha$ -nitroacetone were studied earlier by Hantzsch<sup>32,339,340</sup> and by others<sup>36,249,331</sup>. Other examples have been studied more recently<sup>333,341</sup>. The nitronic acid appears to be the least favored form at equilibrium. The keto form predominates (ca. 99%) in protic and aprotic solvents for aromatic and aliphatic acyclic nitro ketones.

The properties of alicyclic  $\alpha$ -ketonitronic acids (**91**) generally resemble those of their acyclic counterparts. Alkali salts of alicyclic  $\alpha$ -ketonitronic acids (**90**) have been prepared frequently since they are readily available by alkaline nitration of ketones<sup>329,330</sup>. An oil is obtained by acidification of the  $C_6$  potassium salt (**90**,  $n = 4$ ) with dilute sulfuric acid at  $0^\circ$ ; the oil, possibly a mixture of tautomers

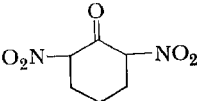
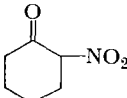
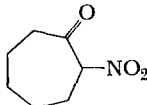
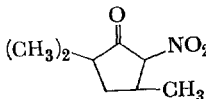
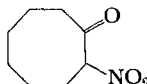
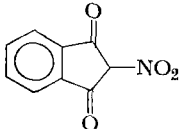
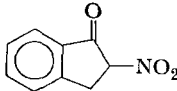
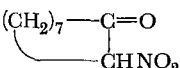


**91**, **92**, and **93** (equation 98), slowly crystallizes on standing to form  $\alpha$ -nitrocyclohexanone (**92**,  $n = 4$ ; m.p.  $39.5-40^\circ$ )<sup>329</sup>. Solutions of the freshly prepared oil give a red color with ferric chloride and are acidic.

In solution in aprotic solvents alicyclic  $\alpha$ -nitrocycloalkanones appear to exist to some extent in the enol form **93**<sup>334,342</sup>. However, in protic solvents the keto form is strongly favored (Table 10). Ring size affects the enol content in carbon tetrachloride solution<sup>330</sup>;  $C_6$ ,  $C_8$ , and  $C_{10}$   $\alpha$ -nitrocycloalkanones have higher enol contents than  $C_7$ ,  $C_9$ , and  $C_{12}$  homologs.

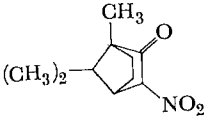
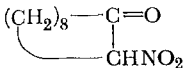
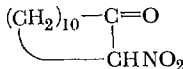
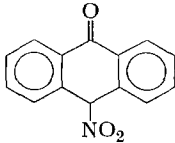
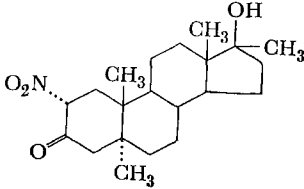


TABLE 10. Equilibrium composition of nitroketones.

Nitroketone	Solvent	% Keto	Ref.
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_2\text{NO}_2$	$\text{CCl}_4$	100	333
$\text{CH}_3\text{CH}_2\text{COCH}(\text{CH}_3)\text{NO}_2$	$\text{CCl}_4$	100	333
$\text{CH}_3\text{COC}(\text{CH}_3)_2\text{NO}_2$	$\text{CCl}_4$	100	333
	$\text{CH}_2\text{Cl}_2$	25	335
	$(\text{CD}_3)_2\text{SO}_2$	100	335
	$\text{EtOH}$	100	335
	$\text{CCl}_4$	50	330
	$\text{CDCl}_3$	69.4	333
	$\text{CCl}_4$	100	330
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}(\text{C}_2\text{H}_5)\text{NO}_2$	$\text{CCl}_4$	100	330
$\text{C}_6\text{H}_5\text{COCH}_2\text{NO}_2$	$\text{C}_6\text{H}_5\text{CH}_3$	89.7	36
	$\text{C}_2\text{H}_5\text{OH}$	94.7	36
	$\text{CH}_3\text{OH}$	97.2	36
	$\text{CDCl}_3$	100	333
	$\text{CCl}_4$	100	330
	$\text{CCl}_4$	70	330
	$\text{H}_2\text{O}$	2	336
	$\text{EtOH}$	10	336
	$\text{CH}_3\text{CO}_2\text{H}$	12	336
	$\text{Et}_2\text{O}$	62	336
	$\text{C}_6\text{H}_6$	90	336
	$n\text{-C}_6\text{H}_{14}$	10	330
	$\text{CCl}_4$	70	330
	$\text{EtOH}$	70	330
$\text{C}_6\text{H}_5\text{COCH}(\text{CH}_3)\text{NO}_2$	neat	100	333
	$\text{CCl}_4$	90	330

(continued)

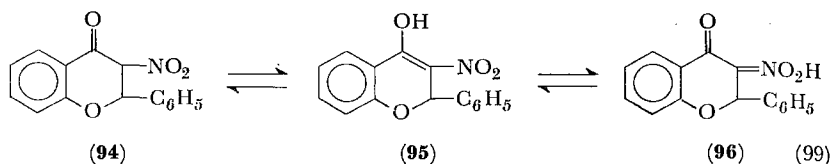
TABLE 10—*continued*

Nitroketone	Solvent	% Keto	Ref.
	$\text{C}_6\text{H}_6$ $\text{D}_2\text{O}$	93 100	337 337a
	$\text{CCl}_4$	60	330
	$\text{CCl}_4$	100	330
	EtOH	97	35
	$\text{CDCl}_3$	50	334

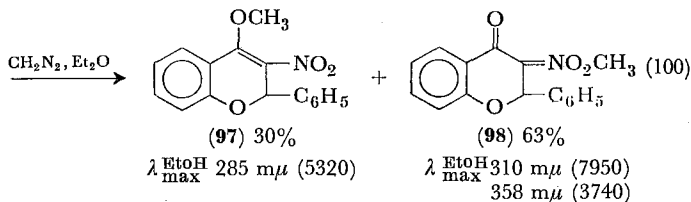
Spectroscopic evidence strongly supports the presence of the enol **93** rather than nitronic acid form **91** in aprotic solvents<sup>330</sup>. For  $\alpha$ -nitrocyclohexanone a sharp OH peak at  $-3.6 \tau$  ( $\text{CCl}_4$ ), intensity  $\cong 0.5$  proton, is observed in the nmr spectrum of the equilibrated mixture. In addition there appears a weak band at  $1613 \text{ cm}^{-1}$  in the neat sample (possible  $\text{C}=\text{C}$ ), and  $\text{NO}_2$  bands at  $1550$  and  $1515 \text{ cm}^{-1}$  representing unconjugated and conjugated nitro groups, respectively. Other  $\alpha$ -nitrocycloalkanones ( $\text{C}_7$ – $\text{C}_{12}$ ) have similar spectra. The carbonyl band appears in *reduced* intensity near  $1720$ – $1740 \text{ cm}^{-1}$  in carbon tetrachloride solution indicating presence of  $\alpha$ -nitroketone **92** rather than  $\alpha$ -ketonitronic acid **91**; also the latter might be expected to have a carbonyl band near  $1639 \text{ cm}^{-1}$  as found in the salts **90**. No sharp OH stretching bands are found in the infrared spectra; only very broad bands, characteristic of more

associated protons, occur. The ultraviolet spectrum of  $\alpha$ -nitrocyclohexanone in carbon tetrachloride reveals a strong band at  $320\text{ m}\mu$  ( $\epsilon\ 3970$ )<sup>330</sup>. Other  $\alpha$ -nitrocycloalkanones ( $C_7$ - $C_{12}$ ) have similar ultraviolet spectra ( $\lambda_{\text{max}}$   $320$ - $370\text{ m}\mu$ ;  $\epsilon_{\text{max}}$   $1700$ - $4000$ ), which could be assigned to the enol form<sup>330</sup>. Alkali salts of  $\alpha$ -nitroketones also have strong bands at ca.  $340\text{ m}\mu$  ( $\epsilon\ 12000$ ) in absolute ethanol<sup>330</sup>.

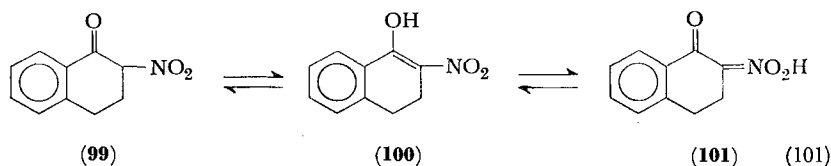
Comparison of the ultraviolet spectra of the  $\alpha$ -nitroketone **94** with that of its nitronic ester **98** and enol ether **97** (prepared by reaction of **94** with diazomethane) indicate very little keto form to exist in 96% ethanol solution<sup>343-345</sup> (equations 99, 100). However, the relative concentrations of enol **95** and nitronic acid **96** cannot be



(94, 95, 96):  $\lambda_{\text{max}}^{\text{EtOH}}$  255(8450), 328 (4970), and 378 (11,100)  $\text{m}\mu$



determined from the ultraviolet spectral data alone. 2-Nitro-1-tetralone (**99**) exhibits behavior different ~~than~~<sup>from</sup> that of **94**. It exists in the enol form in hexane, but in ethanol the keto form predominates<sup>330</sup>. The band at  $370\text{ m}\mu$  is not found in 2-bromo-2-nitro-1-tetralone or 1-tetralone and is believed to be characteristic of the enol form **100** rather than the nitronic acid, **101**<sup>330, 334</sup> (equation 101),

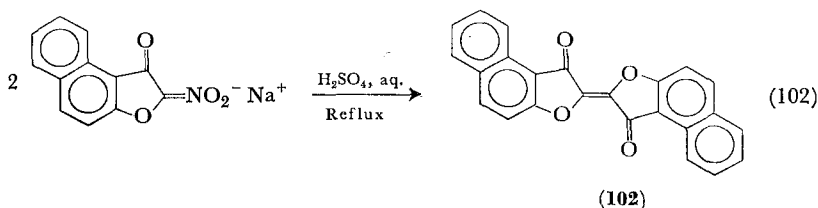


(99, 100, 101):  $\lambda_{\text{max}}^{\text{EtOH}}$  370  $\text{m}\mu$  (294);  $\lambda_{\text{max}}^{\text{Hexane}}$  370  $\text{m}\mu$  (10,800)

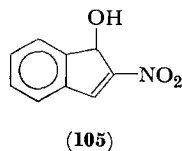
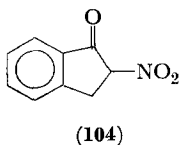
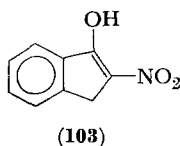
The formation of oxindigos (e.g. **102**) by heating acidified

$\alpha$ -ketonitronate salts suggests a radical-anion coupling reaction characteristic of nitronic acids whose anions are resonance stabilized<sup>332,346</sup> (equation 102).

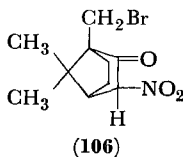
The enol form **103** of 2-nitro-1-indanone (**104**) described by earlier workers<sup>347,348</sup> has recently been shown to have the isomeric



nitroolefin structure **105**<sup>349,350</sup>. The substance is prepared by condensation of *o*-phthalaldehyde with nitromethane.

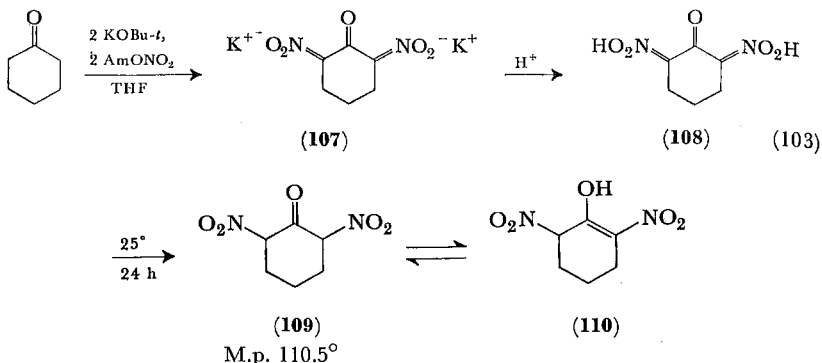


$\alpha$ -Nitrocamphor and certain bromo and chloro derivatives have been studied extensively<sup>337,351-362</sup>. With *pseudo* bromonitrocamphor (**106**) two forms have been isolated, m.p. 108° and 142°; the higher melting form is said to be a nitronic acid<sup>337,353,355</sup>. However, the various crystalline so-called *aci* forms could also be epimeric nitro



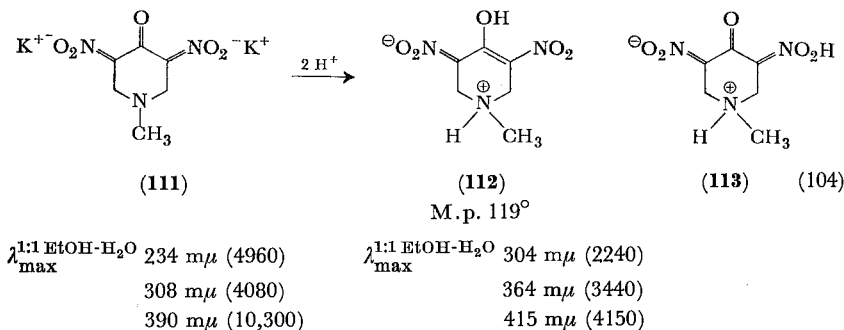
ketones<sup>362</sup>. The mutarotation of  $\alpha$ -nitrocamphor is catalyzed by acids and bases<sup>357,362</sup>; general acid catalysis is observed<sup>362</sup>.

Salts of alicyclic  $\alpha, \alpha'$ -dinitronic acids (e.g. **107**) have been prepared from cycloalkanones by reaction with alkyl nitrates and alkali alkoxides<sup>192,329,335,363</sup>. Acidification of salt **107** produces an oil described as a bisnitronic acid **108**<sup>329</sup>, but which may contain ketone **109**, enol **110**, as well as a nitronic acid derived from **110**. On standing, the oil slowly crystallizes forming ketone **109**. In methylene chloride solution **109** appears to exist 75% as the enol form **110**, but in ethanol solely as ketone **109**<sup>335</sup> (equation 103).

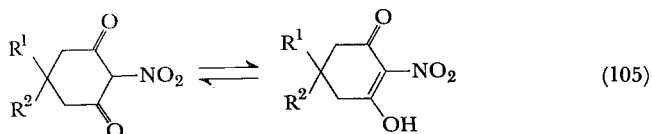


Dipotassium cyclopentanone-2,5-bisnitronate on acidification gave crystals (not identified) which decomposed readily to produce an oil<sup>329</sup>.

Extending this reaction to N-methyl-4-piperidone produced a zwitterion (**112**) on acidification of the bisnitronate salt (**111**)<sup>192</sup>. Its structure is believed to be the enol **112**, rather than the keto-nitronic acid **113** since its spectra are different from the disalt **111**. The carbonyl band of **111** at  $1600 \text{ cm}^{-1}$  (Nujol) is not found in **112**, and **112** has a broad OH band near  $2750 \text{ cm}^{-1}$  and an ultraviolet band at  $364 \text{ m}\mu$  not found in **111** (equation 104).



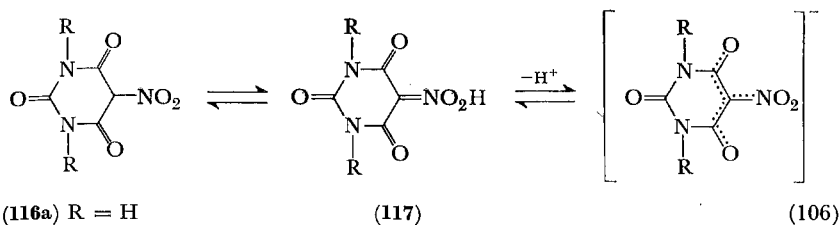
Alicyclic  $\alpha, \alpha'$ -diketonitro compounds **114–118** have been prepared<sup>54, 336, 339, 364–376</sup>. These substances are rather strong acids and in solution in protic solvents exist largely as resonance stabilized nitronate anions. The 2-nitro-1,3-cyclohexanedione derivatives **114a** and **114b**, have been described as nitroenols **115a, b** in the solid state<sup>374</sup> (equation 105). The strong absorption bands at  $293 \text{ m}\mu$  ( $\epsilon$  5000) and at  $296 \text{ m}\mu$  ( $\epsilon$  7000) of chloroform solutions of **114a**

(114a)  $\text{R}^1 = \text{R}^2 = \text{CH}_3$ 

(115a,b)

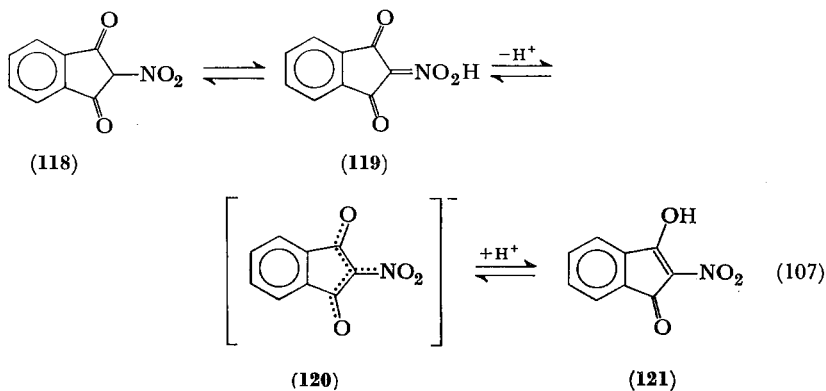
(114b)  $\text{R}^1 = \text{H}; \text{R}^2 = \text{C}_6\text{H}_5$ 

and **114b**, respectively, suggest a high concentration of enol in the aprotic solvent. 2-Nitrodimedone (**114a**) is a relatively weak acid ( $\text{p}K_{\text{a}}^{\text{Nitro}} \cong 3$ ) compared to nitrobarbituric acid (**116a**) and 2-nitro-1,3-indanedione (**118**,  $\text{p}K_{\text{a}}^{\text{Nitro}} < 0$ )<sup>54,339,365,369</sup>. Nitrobarbituric acid (**116a**) and its dimethyl derivative (**116b**, m.p.  $152^\circ$ ) were

(116a)  $\text{R} = \text{H}$ (116b)  $\text{R} = \text{CH}_3$ M.p.  $152^\circ$ 

prepared and studied by Holleman<sup>54</sup> who described them as nitronic acids **117** (equation 106).

2-Nitro-1,3-indanedione (**118**), a much studied compound<sup>366-376</sup>, is a strong acid, comparable to hydrochloric<sup>365,369</sup>. It cannot be acetylated<sup>365</sup> and in water exists only 2% in the nitrodiketo form **118**, or 98% as forms **119-121** by bromine titration<sup>336</sup>; in benzene

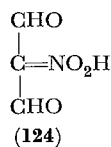
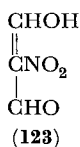
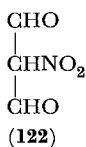


(120)

(121)

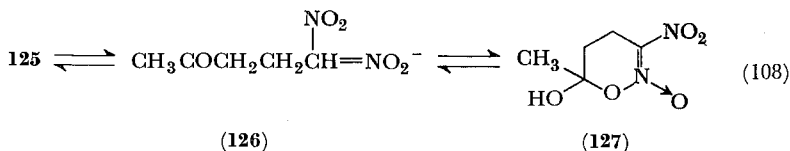
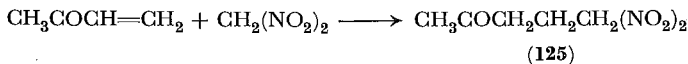
solution, however, it exists 90% in the nitrodiketo form **118** (equation 107). This interesting solvent effect is opposite to that found for all other  $\alpha$ -nitroketones. Usually the nitroketone form is favored in protic solvents and the enol form is favored in aprotic solvents. It appears that the enol form **121** in this unique system is not important in either protic or aprotic solvents; the ionic form **120** is evidently very important in protic solvents.

Nitromalonaldehyde (**122**, **123**) is an unstable substance, m.p. 50–51°<sup>377</sup>. It is prepared by acidification of its silver salt with ethereal hydrogen chloride<sup>377</sup>. In water it produces a yellow, strongly acidic solution, but it decomposes rapidly in this solvent to yield 1,3,5-trinitrobenzene and formic acid. It is soluble in benzene and may be crystallized from ligroin. In the solid state and in



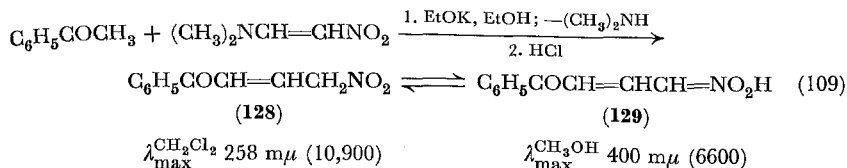
aprotic solvents it probably exists principally as the enol **123**. Very little nitronic acid **124** would be present in protic solvents. Rather, one would find principally the anion since this is a strong acid ( $\text{p}K_{\text{a}}^{\text{Nitro}} \cong 0$ ). The sodium salt is nearly colorless in the solid state and relatively stable<sup>378,379</sup>. Aqueous solutions of nitromalonaldehyde, however, are colored yellow.

$\gamma$ -Ketonitronic acids are known. Some are readily prepared by Michael addition of vinyl ketones to suitable nitroalkanes<sup>375,380,381</sup>. The slow rate of reduction of the carbonyl group of **125** with sodium borohydride may be explained by formation of the cyclic *pseudo* ester **127** from  $\gamma$ -ketonitronate anion **126**<sup>381</sup> (equation 108). Some ketonitronic acid might be expected to be present in the aqueous methanol which was employed as solvent.



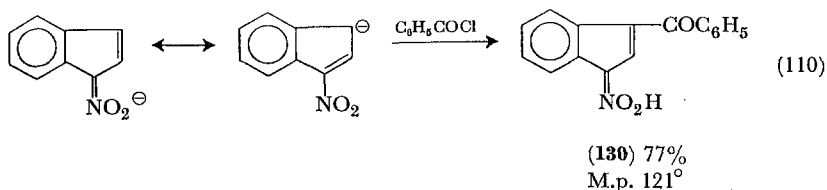
The nitrovinylation reaction<sup>191,213,382</sup> leads to 4-keto-1-nitroolefins which exist principally in the nitronic acid form in protic

solvents, and principally in the nitro form in aprotic solvents<sup>213,219</sup>. The compound **128** in methylene chloride solution has the characteristic phenyl vinyl ketone absorption (e.g.  $\text{C}_6\text{H}_5\text{COCH}=\text{CHCH}_3$

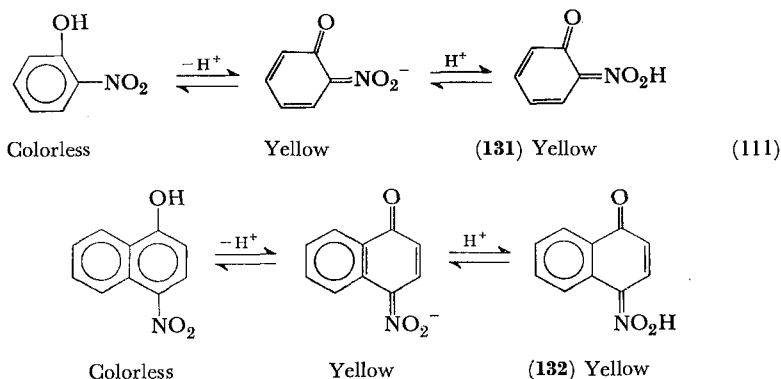


$\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  256 m $\mu$ ,  $\epsilon_{\text{max}}$  17,400) and absorbs at much lower wave length than the nitronic acid **129**, with its extended conjugation, which is formed in methanol (equation 109). Unlike compound **125** the carbonyl group in **128** can be easily reduced to hydroxyl with sodium borohydride<sup>213</sup>.

The benzoylindenenitronic acid **130** is known and is prepared by acylation of potassium indene-1-nitronate<sup>86</sup> (equation 110).



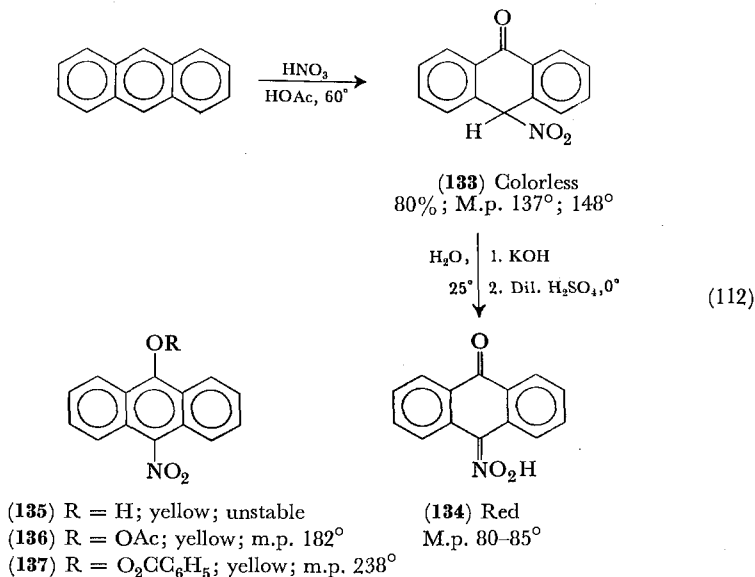
The tautomers of *o*- and *p*-nitrophenols are  $\alpha$ - and  $\gamma$ -ketonitronic acids, respectively<sup>383,384</sup>. Their yellow color in basic solution in protic solvents is due to nitronate anions. The yellow color was observed by Hantzsch to remain momentarily on acidification of these salts due to formation of the relatively weak nitronic acids **131**, **132**<sup>383,384</sup> (equation 111); esters of these acids have been prepared<sup>384</sup>.





Tautomerization of the yellow nitronic acids **131**, **132** to the colorless nitrophenols occurs very rapidly.

Anthrone-10-nitronic acid (**134**) is an interesting  $\gamma$ -ketonitronic acid<sup>35, 385, 386</sup>. Two tautomeric forms have been reported—nitro ketone **133** and nitrophenol **135**. Colorless 10-nitroanthrone (**133**) is prepared by nitration of anthracene in acetic acid. It forms a deep red potassium salt when treated with potassium hydroxide solution.



The salt reacts with cold dilute sulfuric acid to yield carmine-red crystals of the ketonitronic acid **134**<sup>386</sup> (equation 112). The nitronic acid is quite stable and may be stored for months in a desiccator. It melts unsharply, ca. 80–85°, with decomposition, ultimately forming anthraquinone on continued heating<sup>386</sup>. On standing with water or dilute acids it is converted into the nitro form **133** with formation of some anthraquinone<sup>386</sup>. The nitronic acid or its potassium salt can be brominated to form colorless 10-bromo-10-nitroanthrone, m.p. 116°<sup>386</sup>. Reaction of the silver salt of **134** with methyl iodide produced a resin from which only anthraquinone could be isolated<sup>386</sup>. The red potassium nitronate salt may be acetylated or benzoylated to produce yellow 10-nitro-9-anthryl acetate (**136**) or benzoate, **137**<sup>35</sup>. 10-Nitro-9-anthrol (**135**, an unstable yellow substance, isolable only at –5°) was prepared by Hantzsch<sup>385</sup> by acidification of the ammonium salt of **134** with hydrogen chloride in ether at Dry Ice temperature; evaporation of the yellow solution gave **135**. On

warming to room temperature **135** immediately produced the red nitronic acid **134**.

## IV. NITRONIC ACID ESTERS

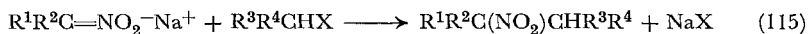
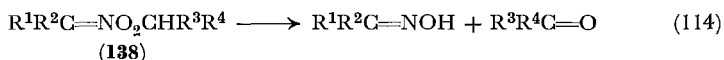
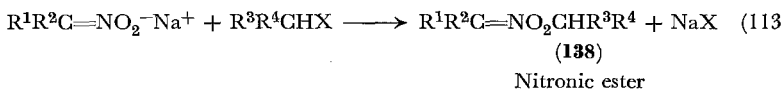
### A. Preparation of Nitronic Acid Esters

The various methods available for preparing the rather unstable nitronic acid esters are presented in this section. Acyclic and cyclic esters (e.g. the 2-isoxazoline *N*-oxides) are considered separately. Certain side reactions which defeat the syntheses are discussed, including C-alkylation of nitronates.

#### I. Acyclic nitronic acid esters

Three principal methods are available for preparation of acyclic nitronic esters: (a) alkylation of sodium or potassium nitronate salts, (b) alkylation of silver nitronate salts, and (c) reaction of nitroalkanes and nitronic acids with diazomethane.

The O-alkylation of sodium and potassium nitronate salts has been examined extensively<sup>5,23,84,275,387-393</sup>. The initial product is a nitronic ester (**138**; equation 113), which may decompose easily under the reaction conditions to form an oxime and an aldehyde or ketone (equation 114). C-Alkylation may also occur (equation 115). The course of the reaction depends on the structures of the



nitronate salt and alkylating agent. Alkylating agents of various types have been employed, including alkyl fluoroborates<sup>23,390,391</sup>, sulfates<sup>275,394-396</sup>, and halides<sup>65,196,387-389,392,393,396,397</sup>. Nitronic esters prepared by this method are listed in Table 11 (method A).

O-Alkylation with alkyl fluoroborates is the best method when alkali metal nitronate salts are employed<sup>23,390,391</sup>. In a procedure developed by Kornblum and coworkers<sup>23,391</sup>, nearly quantitative yields are obtained in a rapid reaction at 0° (equation 116).

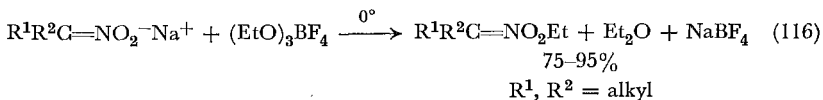
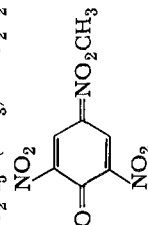


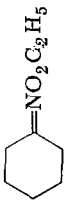
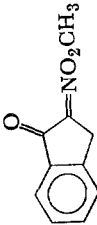
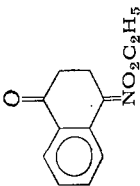
TABLE 11. Synthesis and properties of acyclic nitronic esters.

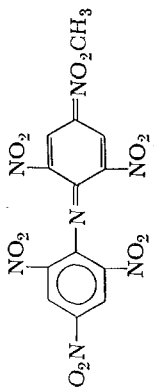
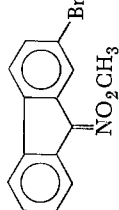
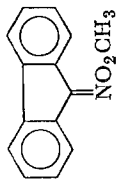
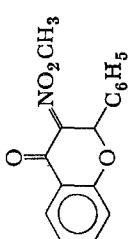
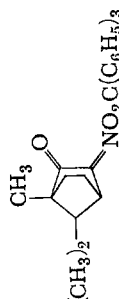
Nitronic ester	Synthetic method <sup>a</sup>	Yield (%)	M.p., (°C)	Half-life (approx.) <sup>b</sup> at 25°	Ref.
$(\text{NO}_2)_2\text{C}=\text{NO}_2\text{CH}_3$	A, C	—	dec. <sup>c</sup>	few min	398, 399
$\text{O}_2\text{NCH}=\text{NO}_2\text{CH}_3$	C	—	dec. <sup>c</sup>	few min	400
$\text{NCC}(\text{NO}_2)=\text{NO}_2\text{CH}_3$	B	58	62–64	—	401, 402
$(\text{NO}_2)_2\text{C}=\text{NO}_2\text{C}_2\text{H}_5$	A, C	—	dec. <sup>c</sup>	few min	398
$\text{H}_2\text{NCOCH}=\text{NO}_2\text{CH}_3$	B	—	112°	—	403
$\text{CH}_3\text{CH}=\text{NO}_2\text{CH}_3$	A	90–95	liquid	3–24 h	23
$\text{H}_2\text{NCOCH}=\text{NO}_2\text{C}_2\text{H}_5$	B	30	114	several h.	403
$\text{CH}_3\text{C}(\text{NO}_2)=\text{NO}_2\text{C}_2\text{H}_5$	B	—	dec.	few h	15
$\text{CH}_3\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	A	94	liquid	1 day	23
$\text{NCC}(\text{CONH}_2)=\text{NO}_2\text{C}_2\text{H}_5$	B	—	—	few h	15, 404–406
$\text{C}_2\text{H}_5\text{O}_2\text{CCH}=\text{NO}_2\text{CH}_3$	B, C	—	b.p. 84°/2.5 mm	—	394, 407
$\text{CH}_3\text{CH}_2\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	A	79	liquid	1 day	23
$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{C}_2\text{H}_5$	A	75–80	liquid	few h	23
$(\text{NC})_2\text{C}=\text{CHCH}=\text{NO}_2\text{CH}_3$	B	65	105	—	191
$(\text{CH}_3\text{O}_2\text{C})_2\text{C}=\text{NO}_2\text{CH}_3$	C	90	68	—	394, 408
$\text{C}_2\text{H}_5\text{O}_2\text{CCH}=\text{NO}_2\text{C}_2\text{H}_5$	B	40	b.p. 81°/3 mm	—	407
$\text{H}_2\text{NCOCH}=\text{NO}_2\text{C}_3\text{H}_7-n$	B	32	107	—	403, 409
$n\text{-C}_3\text{H}_7\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	A	90–95	liquid	1 day	23
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{NO}_2\text{C}_2\text{H}_5$	A	90–95	liquid	5 min	23
	B	—	40–42	few min	384

	B	—	—5	few min	384
	B	—	—	few min	384
$(\text{NO}_2)_2\text{C}=\text{NO}_2\text{CH}_2\text{C}_6\text{H}_4-\text{NO}_2-4$	B	—	—	few min	410
	B	1.5	50-52	few min	384
4-BrC <sub>6</sub> H <sub>4</sub> CH=NO <sub>2</sub> CH <sub>3</sub> ('trans')	C	80	66.5-67.5	2 weeks	23, 394
4-BrC <sub>6</sub> H <sub>4</sub> CH=NO <sub>2</sub> CH <sub>3</sub> ('cis')	C	20	—	few h	23
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=NO <sub>2</sub> CH <sub>3</sub> ('trans')	C	67	118-120	several weeks	23
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=NO <sub>2</sub> CH <sub>3</sub> ('cis')	C	33	—	several h	23
	B	—	—	few min	410
C <sub>6</sub> H <sub>5</sub> CH=NO <sub>2</sub> CH <sub>3</sub>	A, C	—	liquid	3-4 h	394, 395
C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> CH=NO <sub>2</sub> CH <sub>3</sub>	C	17	54.5	1 week	297
H <sub>2</sub> NCOCH=NO <sub>2</sub> C <sub>5</sub> H <sub>11-n</sub>	B	28	100	—	403
(CH <sub>3</sub> O <sub>2</sub> C) <sub>2</sub> C=CHCH=NO <sub>2</sub> CH <sub>3</sub>	B	70	87	—	191

(continued)

TABLE 11—continued

Nitronic ester	Synthetic method <sup>a</sup>	Yield (%)	M.p., (°C)	Half-life (approx.) <sup>b</sup> at 25°	Ref.
	A	100	liquid	1-5 min	23
2-BrC6H4C(CN)=NO2CH3	B	—	104-105	few h	193
4-BrC6H4C(CN)=NO2CH3	B	70-80	110	several h	196
2,4,6-Cl3C6H2N2C(CH3)=NO2CH3	C	29	89-90	—	299
C6H5C(CN)=NO2CH3	B	50-70	41-42	several h	194, 411, 412
2,4-Cl2C6H3N2C(CH3)=NO2CH3	C	40	110-111	—	299
C6H5COCH=NO2CH3	C	—	liquid	—	394
4-BrC6H4CH=NO2C2H5	A	95	35-40	1-3 h	23
('trans'/'cis' = 3/1; mixture)					
4-ClC6H4N2C(CH3)=NO2CH3	C	—	112	—	298
4-CH3C6H4SO2CH=NO2CH3	C	—	liquid	—	394
4-O2NC6H4CH=NO2C2H5 ('trans')	A	74	100-101	several weeks	23
4-O2NC6H4CH=NO2C2H5 ('cis')	A	18	—	few h	23
C6H5N2C(CH3)=NO2CH3	C	65	71.5-72	several h	6, 298
4-BrC6H4COCH=CHCH=NO2CH3	C	35	128	—	213
C6H5C(CN)=CHCH=NO2CH3	C	38	68	—	191
C6H5COCH=CHCH=NO2CH3	C	28	118	—	213
	C	40	132	—	213
	B	—	—	few min	384

$4\text{-CH}_3\text{OC}_6\text{H}_4\text{COCH=CHCH=NO}_2\text{CH}_3$	C	32	111-118	—	213
	B	poor	140-141	few h	413
	B	—	72-80	few min	204
	A	—	84	—	275
$\text{C}_6\text{H}_5\text{N}_2\text{C}(\text{C}_6\text{H}_5)=\text{NO}_2\text{CH}_3$	C	17	92	—	295
	C	63	—	—	344
	A	44	149-152	—	414

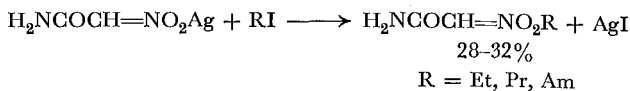
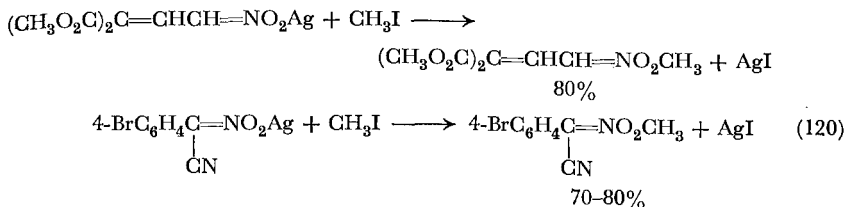
<sup>a</sup> Methods of synthesis: A. Alkylation of sodium or potassium nitronate salt. B. Alkylation of silver nitronate salt. C. Diazomethane reaction with nitroalkane or nitronic acid.

<sup>b</sup> Very approximate time for half of undiluted sample to decompose.

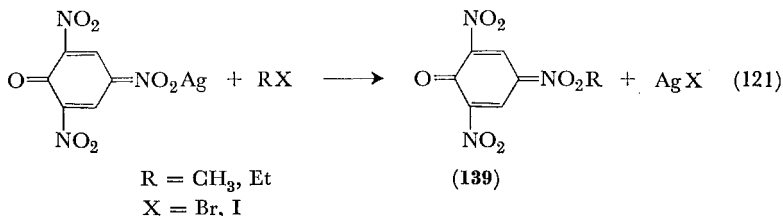
<sup>c</sup> Isolated in solution only. Ester decomposes on attempted isolation by removal of solvent.

In contrast to the behavior of alkali nitronate salts, the reaction of silver nitronate salts with alkyl halides can be used to prepare nitronic esters<sup>15,191,193,194,196,306,384,386,387,401,403-408,410-413</sup>. As a synthetic method it appears limited to electronegatively substituted

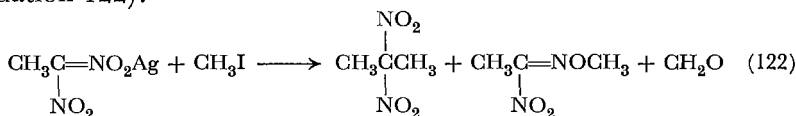
salts. Methyl and other alkyl iodides have been employed more frequently than bromides or chlorides (ether solvent) to produce nitronic esters (Table 11, method B) (equation 120). Silver picrate



led to a very low yield of the unstable methyl or ethyl ester, **139**<sup>384,386</sup> (equation 121). As with alkali nitronate salts, certain silver nitronates react with alkyl halides to produce C-alkylation products and/or



oximes, oxime ethers, and aldehydes or ketones<sup>15,407,410,415-418</sup> (equation 122).

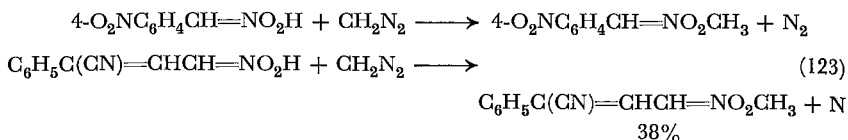


Methyl nitronic esters are conveniently obtained by reaction of nitronic acids with diazomethane in ether solvent (*direct method*). More conveniently, certain acidic nitroalkanes may be used as reactant (*indirect method*). The diazomethane reaction has the advantage that mild conditions may be employed, and C-alkylation products are not obtained. Oximes can result, however, by decomposition of the ester<sup>394</sup>. Nitronic esters prepared by reactions of diazomethane are listed in Table 11, method C.

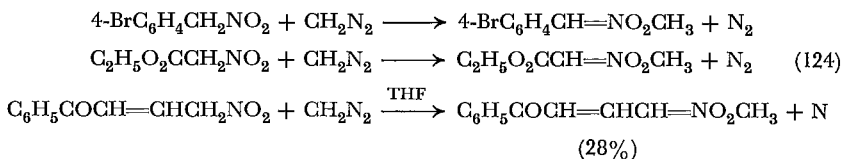
The *direct method* which requires a nitronic acid reactant has seldom been employed<sup>23,191,394</sup>, but would appear to be potentially quite useful. It is applicable at low temperature, and, although not yet



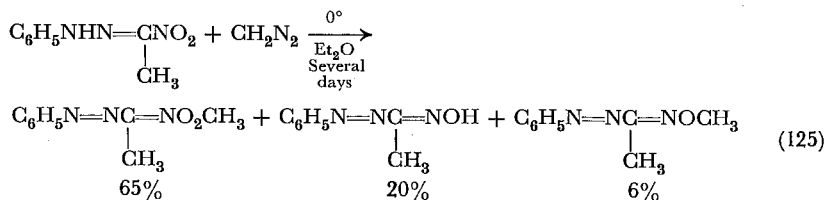
exploited, should be applicable to those nitronic acids derived from more weakly acidic nitroalkanes which do not react with diazomethane. 4-Nitro, 4-bromophenyl- and phenylmethanenitronic acid have been converted into their methyl esters; the parent nitroalkanes also react to give the same product<sup>23,394</sup> (equation 123).



The *indirect method* is quite effective with negatively substituted nitroalkanes ( $\text{p}K_{\text{a}}^{\text{Nitro}} < \text{ca. } 8$ )<sup>23,213,344,394,419,420,420a</sup>.  $\alpha$ - and  $\gamma$ -Nitro ketones and carboxylic esters react, but some enol methyl ether formation may be expected to result with some of these compounds (see section III.C.4)<sup>344</sup> (equation 124). More weakly acidic nitroalkanes ( $\text{p}K_{\text{a}}^{\text{Nitro}} > \text{ca. } 8$ ) such as nitromethane, 2-nitrobornane, and 3-phenyl-1-nitropropane do not react with diazomethane<sup>23,421</sup>.

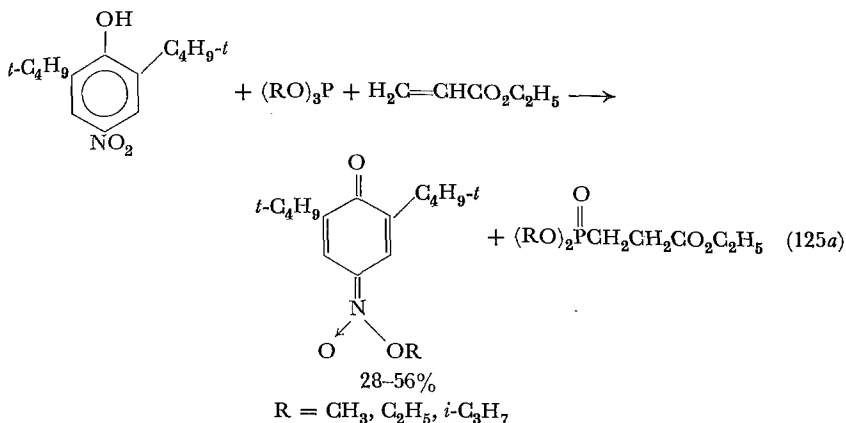


The deeply red-colored  $\alpha$ -arylazonitronic esters may be prepared by reaction of diazomethane with aldehyde 1-nitrohydrazones. Several of these esters have been prepared by Bamberger and coworkers (see Table 11)<sup>6,295-299</sup>. The orange-red hydrazones are readily prepared in high yield by reaction of nitronate salts with diazonium salts at 0° (see section III.C.1.b)<sup>293-296</sup>. Some oxime formation accompanies formation of these unstable esters<sup>298</sup> (equation 125).

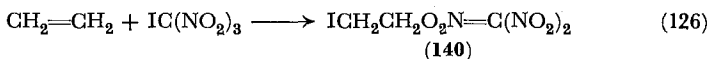


A special method of synthesis of nitronic esters derived from 2,6-di-*t*-butyl-4-nitrophenol employs a trialkyl phosphite and ethyl

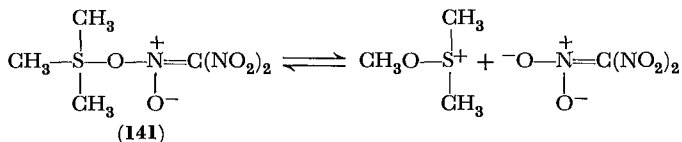
acrylate reacting at room temperature without a solvent (equation 125a)<sup>421a</sup>.



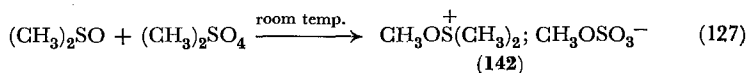
A new, special method of ester preparation is said to involve addition of iodo- or bromotrinitromethane to olefins in a solvent such as dimethyl sulfoxide<sup>399,422–423a,b</sup>, e.g. ethylene and iodotrinitromethane yields **140** (equation 126).



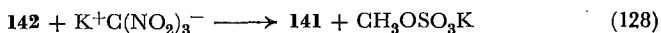
However, recent evidence has shown that the reaction in dimethyl sulfoxide does not lead to simple addition compounds of structure **140**, but rather to compounds of sulfonium structure **141**<sup>423a</sup>. The structure of **141** was proved by synthesis. Dimethyl sulfoxide was



methyated with dimethyl sulfate to compound **142** (equation 127).



Addition of potassium trinitromethane dissolved in dimethoxyethane gave **141** (equation 128).



Nitronic esters have not been prepared by reaction of a nitronic acid with an alcohol.

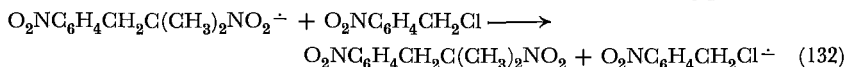
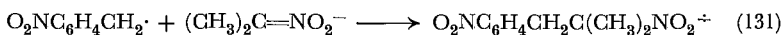
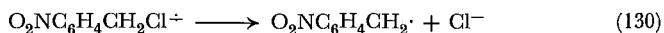
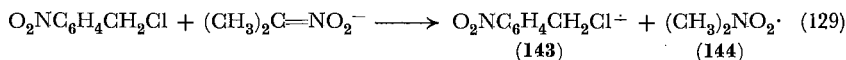
Finally, a comparison of C- and O-alkylation of nitronate salts should be considered at this point<sup>423c</sup>. The extent of C- and O-alkylation is known to depend on three principal factors: (a) the nature of the leaving group in the alkylating agent, (b) the structure of the alkylating agent, and (c) the structure of the nitronate anion. Other factors include nature of the cation and solvent, reaction temperature, and solubility of reactants and products.

The alkylation of alkali nitronate salts has been studied extensively with substituted benzyl alkylating agents (Table 12)<sup>5,314,388,393,397,424-426a,b</sup>. When O-alkylation is the sole reaction, the yield is independent of the nature of the leaving group. However, 2- and 4-nitro substituted benzyl alkylating agents are notably exceptional in their behavior. The extent of C- and O-alkylation of lithium or sodium propane-2-nitronate salts by 2-O<sub>2</sub>N- and 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>X does depend on the nature of the leaving group X. Here, O-alkylation is favored by the best leaving groups.

The extent of C- and O-alkylation depends on the structure of the alkylating agent. 2- and 4-nitrobenzyl chloride<sup>427</sup>, and 2,4-dinitrobenzyl chloride<sup>387</sup> effect principally C-alkylation. However, 3-nitrobenzyl chloride and other benzyl halides effect O-alkylation only<sup>393</sup>.

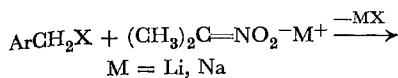
It is to be expected that yields of C- and O-alkylation products would depend on the structure of the nitronate anion. For example, with 4-nitrobenzyl chloride yields of C-alkylation products are: CH<sub>3</sub>CH=NO<sub>2</sub><sup>-</sup> (24 %) and (CH<sub>2</sub>)<sub>5</sub>C=NO<sub>2</sub><sup>-</sup> (62 %)<sup>397</sup>.

Evidence for radical anion intermediates has been obtained by esr measurements in the C-alkylation with 4-nitrobenzyl chloride<sup>314,424,427</sup>. The mechanism in this particular case is considered to be an exchange leading to a radical anion (**143**) and a nitro radical (**144**), followed by loss of chloride ion and coupling in a chain process (equations 129-132)<sup>314,427</sup>.



Supporting this mechanism is the finding that addition of 1,4-dinitrobenzene to this system as an electron scavenger increases the extent of O-alkylation from 6 to 88 %<sup>424</sup>.

TABLE 12. Effect of substituents and leaving group on the extent of C- and O-alkylation of substituted benzyl alkylating agents reacting with sodium and lithium propane-2-nitronate salts.



C-Alkylation  
Product

O-Alkylation  
Products

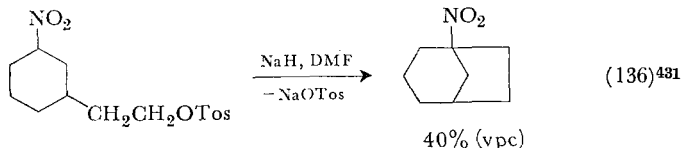
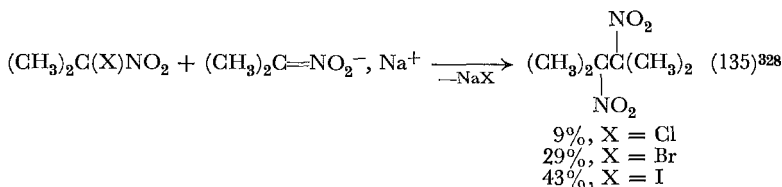
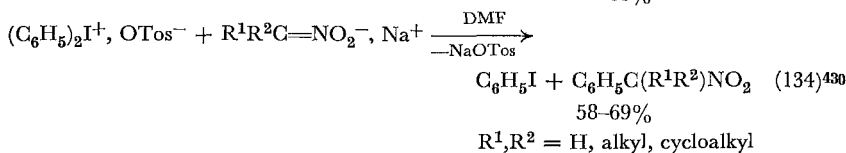
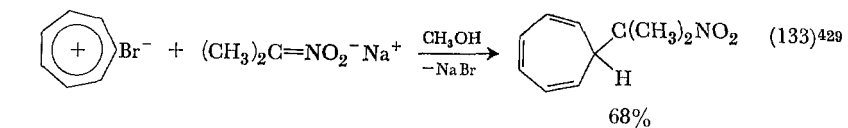
Ar	X	% C-Alkylation	% O-Alkylation <sup>a</sup>	Ref.
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	+N(CH <sub>3</sub> ) <sub>2</sub>	93 <sup>b</sup>	0	424
		90 <sup>c</sup>	0	425
	C <sub>6</sub> Cl <sub>5</sub> CO <sub>2</sub>	93 <sup>b</sup>	0	424, 426
	Cl	92 <sup>b</sup>	6	424, 426
		83 <sup>c</sup>	1	5, 388
	OTos	40 <sup>b</sup>	32	424, 426
	Br	20 <sup>b</sup>	60	422, 426
2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	I	8 <sup>b</sup>	86	424, 426
	Cl	46 <sup>c</sup>	30	388
	Cl	31 <sup>b</sup>	52	424
	Br	1 <sup>b</sup>	98	424
3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Cl	0 <sup>b</sup>	82	424
		— <sup>c</sup>	73	388
	Br	0 <sup>b</sup>	80	424
	I	0 <sup>b</sup>	84	424
2,4-(O <sub>2</sub> N) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	Cl	33 <sup>c</sup>	—	387, 388
	Cl	0 <sup>b</sup>	82–84	424
		0 <sup>c</sup>	73	5
	OTos	0 <sup>b</sup>	82–84	424
	Br	0 <sup>b</sup>	82–84	424
		0 <sup>c</sup>	73	393
	I	0 <sup>b</sup>	82–84	424
4-NCC <sub>6</sub> H <sub>4</sub>	Br	0 <sup>c</sup>	70	5, 393
4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	Br	0 <sup>c</sup>	72	5, 393
4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	Br	0 <sup>c</sup>	77	5
4-(CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup> I <sup>-</sup> C <sub>6</sub> H <sub>4</sub>	I	0 <sup>c</sup>	68	5
4-BrC <sub>6</sub> H <sub>4</sub>	Br	0 <sup>c</sup>	75	5, 393
4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Br	0 <sup>c</sup>	77	5, 393
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Br	0 <sup>c</sup>	70	5
2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Br	0 <sup>c</sup>	68–73	393

<sup>a</sup> Determined by yield of aldehyde, ArCHO, or corresponding acid, ArCO<sub>2</sub>H.

<sup>b</sup> Lithium propane-2-nitronate in dimethylformamide at 0°.

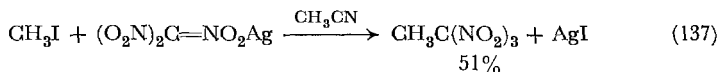
<sup>c</sup> Sodium propane-2-nitronate in ethanol at 25–80°.

Other C-alkylations with various alkylating agents are known (equations 133–136)<sup>328, 428a, b, 429–431</sup>. In these examples, in contrast to the 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>X example, good leaving groups (Br<sup>−</sup>, I<sup>−</sup>,



OTos<sup>−</sup>) favor C-alkylation. Recently, the reaction of equation 135 has been shown to proceed by a radical-anion chain mechanism<sup>314, 428a</sup>.

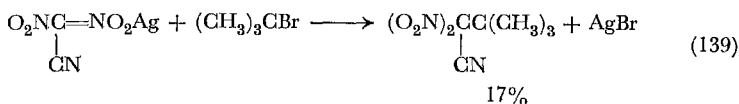
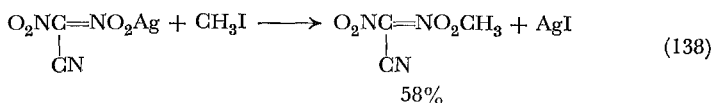
The mechanism of silver dinitromethanenitronate alkylation with alkyl halides has been studied in acetonitrile at 25°<sup>401, 410, 415, 416, 418</sup>. Overall third-order kinetics are observed in a mechanism which involves dinitromethanenitronate anion<sup>418</sup> (equation 137). With the silver salt C-alkylation is limited to primary halides, including allyl



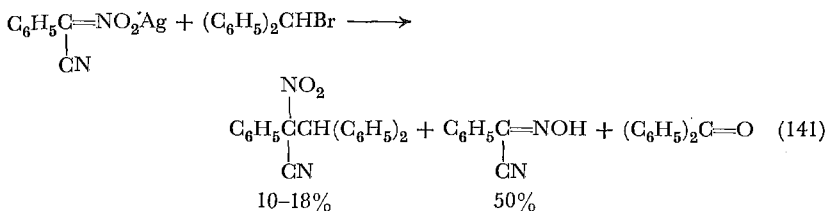
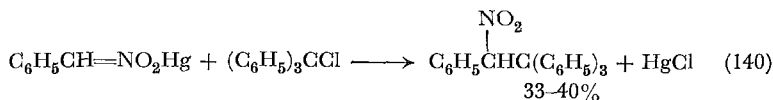
and benzyl halides (28–52% yield)<sup>401, 418, 432</sup>. 2-Bromopropane and other secondary, as well as tertiary halides are believed to undergo O-alkylation; the resulting nitronic esters decompose to yield alkyl nitrate as the principal anomalous product<sup>418</sup>.

Silver nitrocyanomethanenitronate gave a 58% yield of nitronic ester by O-alkylation with methyl iodide (equation 138), but could

also be C-alkylated with *t*-butyl and allyl bromides<sup>418</sup> (equation 139).



C-Alkylation is observed with silver and mercury phenylmethane-nitronate and silver  $\alpha$ -cyanophenylmethanenitronate with diphenylmethyl bromide and trityl chloride<sup>327,387,411,417,433</sup> (equations 140, 141).

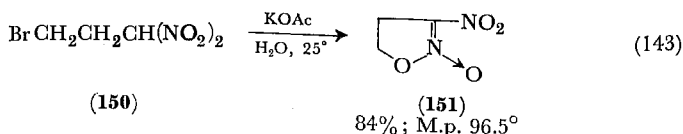


In these particular reactions O-alkylation predominates with the silver salts leading to the nitronic ester decomposition products oxime and ketone.

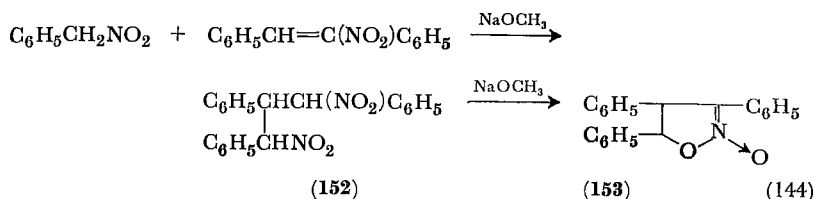
A generalization for the direction of alkylation of ambident anions has been presented by Kornblum<sup>434</sup>. It states that the greater the  $S_N1$  character of the transition state, the greater the preference for bonding to the most electronegative atom in the ambient anion. Because of the instability of nitronic esters it is difficult to test this generalization using the available data on C- vs O-alkylation of nitronates<sup>418,438</sup>. O-Alkylation products (nitronic esters) are thermodynamically less stable than the corresponding C-alkylation products. Also, several routes for ester decomposition are available making it difficult to assess the extent of O-alkylation. With one exception only those nitronic esters having O-*n*-alkyl groups are sufficiently stable to be isolable (Table 11); those having all other types of groups, including secondary and tertiary O-alkyl groups, decompose. On the other hand, stable C-alkylation products have been obtained (usually in low to moderate yields) with a variety of



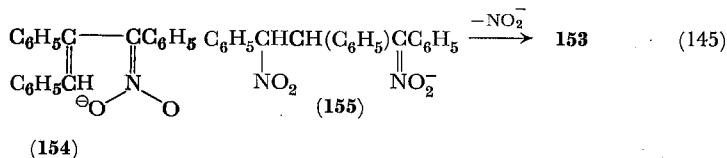
The reaction has been extended to 3-bromo-1,1-dinitroalkanes (Table 13)<sup>436</sup>. 3-Bromo-1,1-dinitropropane (**150**) reacts with potassium acetate in water to precipitate 3-nitro-2-isoxazoline-2-oxide (**151**)<sup>436</sup> (equation 143).



Use of a 1,3-dinitropropane for cyclic ester synthesis is illustrated with 1,3-dinitro-1,2,3-triphenylpropane (**152**), prepared by Michael addition of phenylnitromethane to  $\alpha$ -nitrostyrene<sup>441, 444a</sup>. One equivalent of sodium methoxide converts the dinitro compound to 3,4,5-triphenyl-2-isoxazoline-2-oxide (**153**) (equation 144).



The mechanism of the isoxazoline synthesis from 3-bromoalkane-1-nitronates is reasonably a bromide displacement by nitronate oxygen. The mechanism departing from 1,3-dinitroalkanes has been shown not to involve nitroolefin intermediate **154**<sup>444a</sup>. The reaction occurs by intramolecular displacement of nitrite ion from the mononitronate anion **155** (equation 145)<sup>444a</sup>.

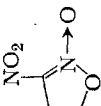
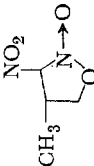
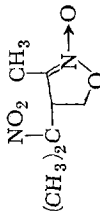
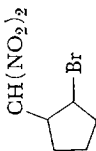
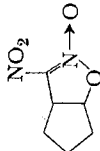


Cyclic nitronic esters with six-membered rings are available from 4-keto-1-nitroalkanes. As discussed in section III.C.4, 4-keto-1,1-dinitropentane is believed to cyclize in solution, although the *pseudo* ester **127** was not isolated.

Michael addition of a 1-nitroalkene to cyclohexane-1,3-dione anion (**156**) (sodium methoxide catalyst) leads to the bicyclic nitronic ester **160**<sup>446</sup> (equation 146).



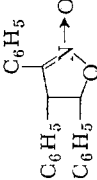
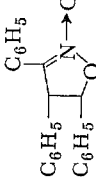
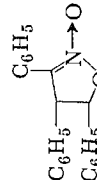
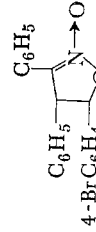
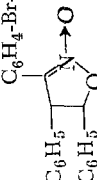
TABLE 13. Synthesis and properties of cyclic nitronic esters (2-isoxazoline *N*-oxides).

Reactant(s)	Base	Nitronic ester	M.p. (°C)	Yield (%)	Ref.
A. Synthesis from 3-halo-1-nitroalkanes					
$\text{BrCH}_2\text{CH}_2\text{CH}(\text{NO}_2)_2$	KOAc		96.5	84	436
$\text{BrCH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NO}_2)_2$	KOH		liquid	95	436
$(\text{CH}_3)_2\text{C}=\text{NO}_2^- \text{Na}^+$ and $\text{CH}_3\text{C}(\text{NO}_2)=\text{CHCH}_2\text{Cl}$	none added		77-78	35-40	408
	KOH		83-83.5	32	436

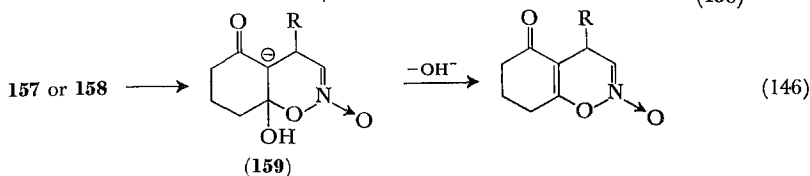
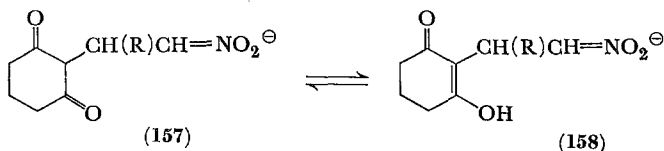
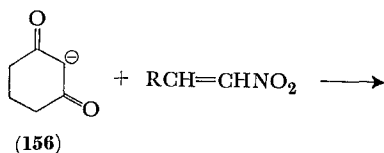
	KOH		94-95	45	436, 423b
$C_6H_5CH(CH_2Br)CH(NO_2)_2$	KOH		80	75	436
$(EtO_2C)_2C(Br)CH(C_6H_5)CH(C_6H_5)CH(NO_2)_2$	KOAc		107-108	90	437, 438
$C_6H_5COCHBrCH(C_6H_5)CH(C_6H_5)CH(NO_2)_2$	KOAc		123	95	26
B. Synthesis from 1,3-dinitroalkanes					
$C_6H_5CH[CH(NO_2)CO_2Et]_2$	$Et_2NH$		181	80 <sup>a</sup>	439, 440

(continued)

TABLE 13—continued

Reactant(s)	Base	Nitronic ester	M.p. (°C)	Yield (%)	Ref.
$C_6H_5CH=C(NO_2)C_6H_5$ and $C_6H_5CH_2NO_2$	$NaOCH_3$		162	45	441
$C_6H_5CH[CH(NO_2)C_6H_5]NH(CH_2)_5$	none added		162	59	442
$C_6H_5CH=CHNO_2$	$(CH_2)_5NH$		162	45	442
$C_6H_5CH=C(C_6H_5)NO_2$ and 4-Br- $C_6H_4CH_2NO_2$	$NaOCH_3$	 4-Br- $C_6H_4$ -Br-4	—	60 (total)	443
			—		

<sup>a</sup> Eight other examples reported (30–90% yield) with  $C_6H_5$  replaced by 4- $CH_3OC_6H_4$ , 4-HOC- $C_6H_4$ , 2-Cl- $C_6H_4$ , 4-Cl- $C_6H_4$ , 2-O<sub>2</sub>NC- $C_6H_4$ , 3-O<sub>2</sub>NC- $C_6H_4$ , 4-O<sub>2</sub>NC- $C_6H_4$ , 2-HO-naphthyl<sup>440</sup>.



(160a) R = CH<sub>3</sub> (52%); m.p. 164–166°

(160b) R = C<sub>6</sub>H<sub>5</sub> (72%); m.p. 165–167°

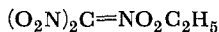
Cyclic nitronic esters having four, seven, eight, and larger membered rings (homologs of 2-isoxazoline *N*-oxides) are unknown. Heterocyclic compounds such as isoxazole and oxadiazole *N*-oxides, etc., may be called cyclic nitronic esters<sup>447, 448</sup>.

Cyclic nitronic esters are not readily prepared by oxidation of the corresponding desoxy compounds (2-isoxazolines, for example<sup>65</sup>)<sup>437</sup>.

### B. Physical Properties of Nitronic Acid Esters

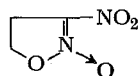
Melting points of nitronic esters are listed in Tables 11 and 13.

The ultraviolet spectra of a few nitronic esters have been reported<sup>23, 401, 402, 409, 449</sup>. None representing the simple aliphatic type, (alkyl)<sub>2</sub>C=NO<sub>2</sub>R are available, but these would be expected to have strong  $\pi - \pi^*$  bands near 220–230 m $\mu$  like the parent nitronic acids (see section III.B). Several  $\alpha$ -nitro acyclic and cyclic esters (e.g. **161**, **162**) have been examined in methylene chloride at 5° and in water solutions<sup>402, 449</sup>. They all have strong absorption of ca. 315–320 m $\mu$ ; the corresponding nitronate anions absorbed at wavelengths 25–50 m $\mu$  higher<sup>402</sup>. The extinction coefficient in the spectrum of unstable ethyl nitroformate (**161**) was obtained by extrapolation to zero time.



(161)

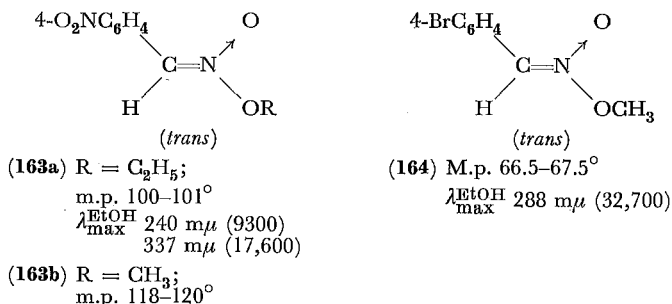
$\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$  315 m $\mu$  (6000)



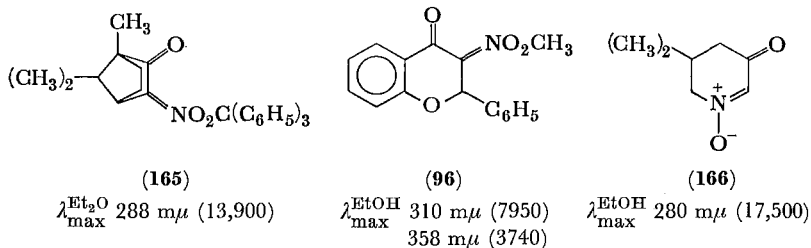
(162)

$\lambda_{\max}^{\text{H}_2\text{O}}$  320 m $\mu$  (8366)

The spectra of the high-melting, presumably *trans* isomers of nitronic esters **163a** and **164** reveal intense absorption near 300 m $\mu$ <sup>23</sup>. The solutions are unstable; the half-life of **164** in 95% ethanol at 19° is ca. 7 days<sup>23</sup>. The half-life of **163a** in deuteriochloroform at room temperature is ca. 2 days<sup>23</sup>.

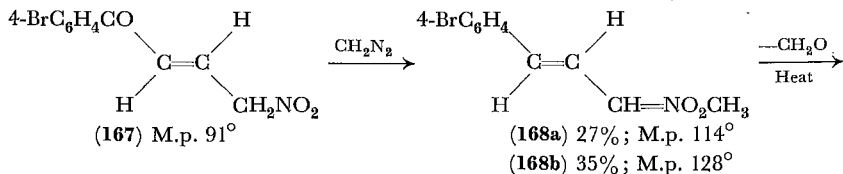


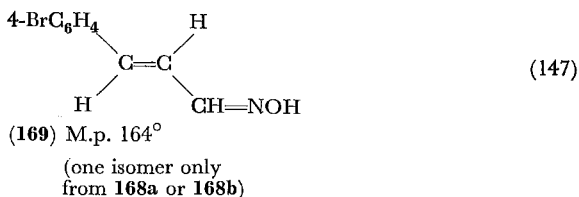
The ultraviolet spectra of  $\alpha$ -keto nitronic esters (**165**, **96**) have been reported; that of **165** resembles that of nitrone **166**<sup>414</sup>.



The infrared spectra of nitronic esters reveal intense C=N absorption in the region 1610–1660 cm<sup>-1</sup> <sup>23,178,408</sup>. This is within the C=N absorption region of nitronic acids (1620–1680 cm<sup>-1</sup>) and oximes (1640–1685 cm<sup>-1</sup>); see section III.B.1.(1).

Examination of the n.m.r. spectra of certain nitronic esters permits stereochemical assignments<sup>23,213</sup>. Like oximes, nitronic esters exist in two geometric forms. Two forms of ester **168** have been isolated by reaction of nitroolefin **167** (presumably *trans*) with diazo-methane<sup>213</sup> (equation 147). Both produce the same oxime **169** by





heating in toluene<sup>213</sup> and are believed to be isomeric about the C=N bond, i.e. *cis* and *trans* forms of the nitronic ester.

The n.m.r. spectra of nitronic esters prepared from primary nitro compounds exhibit vinyl hydrogen peaks near 6.0  $\delta$  for alkyl R in  $\text{RCH}=\text{NO}_2\text{C}_2\text{H}_5$ , and near 7.0  $\delta$  (singlet) for aryl R ( $\text{CDCl}_3$  solvent)<sup>23</sup>. A mixture of *cis* and *trans* isomers is indicated in crude ester samples by noticeable splitting of these peaks. For example, one isomer (probably *trans*) of methyl 4-nitrophenylmethane-nitronate (**163b**), m.p. 118–120°, has a sharp vinyl singlet at 7.20  $\delta$ , whereas crude ester, m.p. 100–108°, clearly containing a mixture of *cis* and *trans* forms, exhibits vinyl singlets at 7.20 and 6.92  $\delta$ <sup>23</sup>. Similar observations were made with the 4-bromo compound **164**. Pure samples of the other (probably lower-melting, *cis*) isomers of **163b** and **164** were not isolated; these isomers were observed (by n.m.r.) to be much less stable than the *trans* isomers; the half-life of *cis*-**164** is estimated at ca. 40 min in deuteriochloroform at room temperature<sup>23</sup>.

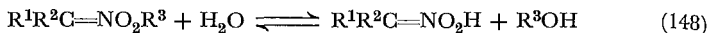
### C. Reactions of Nitronic Acid Esters

Reactions of the rather unstable nitronic esters parallel those of nitronic acids. The same products often are formed from both substances under similar reaction conditions. Hydrolysis under acidic conditions can lead to Nef products or hydroxamic acids. Nitronic esters are good oxidizing agents, are easily reduced, and participate in auto-oxidation-reduction reactions, the most important of these being a disproportionation to an oxime and an aldehyde or ketone. Diene addition, a reaction not yet observed with nitronic acids, leads to 1,2-isoxazolidines with nitronic esters.

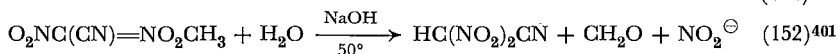
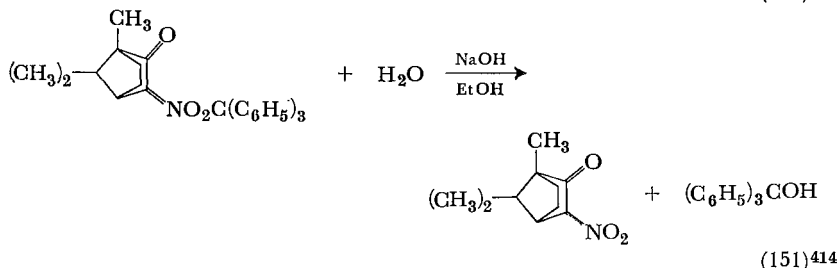
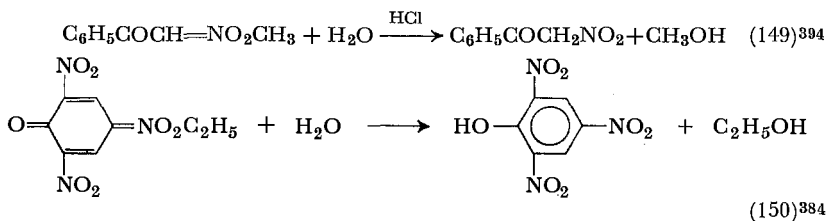
#### I. Hydrolysis of nitronic esters

It seems remarkable that hydrolysis of a nitronic ester to produce an isolable nitronic acid directly (equation 148) has never been

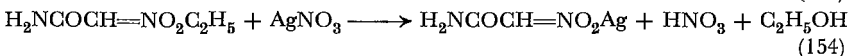
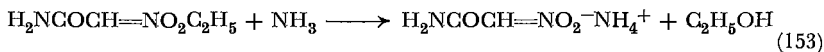
observed. Surprising also is the fact that the reverse reaction, synthesis of a nitronic ester from an alcohol and a nitronic acid, has



not been found. It has been possible, however, to hydrolyze certain nitronic esters (those which form stabilized nitronate anions) to nitroalkanes and alcohols<sup>384,394,401,409,414,421a</sup>. Either acidic or basic catalysts have been employed (equations 149–152).



Ethyl acetamidomethanenitronate reacts with ammonia or silver nitrate to form nitronate salts<sup>403,407</sup> (equations 153, 154).



Acid hydrolysis of nitronic esters under Nef reaction conditions produces aldehydes and ketones (Table 14)<sup>222</sup>. With aliphatic nitronic esters the products and product yields are virtually the same as those obtained from the corresponding nitronic acids (generated from nitronate salts)<sup>47,222,229</sup>. For example, either sodium butane-2-nitronate or ethyl butane-2-nitronate produces 2-butanone in 81–82 % yield when treated with 4*N* sulfuric acid<sup>222,229</sup> (equation 155).

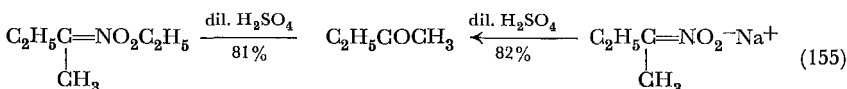


TABLE 14. Reaction of nitronic esters and nitronate salts with sulfuric acid<sup>222</sup>.

## A. Reactions of nitronic esters with sulfuric acid

Nitronic ester	Products with 4N H <sub>2</sub> SO <sub>4</sub> (%)	Products with 31N H <sub>2</sub> SO <sub>4</sub> (%)
4-BrC <sub>6</sub> H <sub>4</sub> CH=NO <sub>2</sub> Et	$\left\{ \begin{array}{l} 4\text{-BrC}_6\text{H}_4\text{CHO (65)} \\ 4\text{-BrC}_6\text{H}_4\text{CONHOH (12)} \end{array} \right\}$	4-BrC <sub>6</sub> H <sub>4</sub> CONHOH (63)
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=NO <sub>2</sub> Et	$\left\{ \begin{array}{l} 4\text{-O}_2\text{NC}_6\text{H}_4\text{CHO (80-82)} \\ 4\text{-O}_2\text{NC}_6\text{H}_4\text{CONHOH (6)} \end{array} \right\}$	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CONHOH (98)
CH <sub>3</sub> CH=NO <sub>2</sub> Et	CH <sub>3</sub> CHO (67)	CH <sub>3</sub> CONHOH (41)
CH <sub>3</sub> CH <sub>2</sub> CH=NO <sub>2</sub> Et	CH <sub>3</sub> CH <sub>2</sub> CHO (good)	—
(CH <sub>3</sub> ) <sub>2</sub> C=NO <sub>2</sub> Et	(CH <sub>3</sub> ) <sub>2</sub> CO (72)	—
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=NO <sub>2</sub> Et	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (good)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CONHOH (42)
CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=NO <sub>2</sub> Et	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub> (81)	—

## B. Reactions of nitronate salts with sulfuric acid

Nitronate salt	Products with 4N H <sub>2</sub> SO <sub>4</sub> (%)	Products with 31N H <sub>2</sub> SO <sub>4</sub> (%)
4-BrC <sub>6</sub> H <sub>4</sub> CHNO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	4-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NO <sub>2</sub> (90) <sup>a</sup>	4-BrC <sub>6</sub> H <sub>4</sub> CONHOH (29)
— 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=NO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NO <sub>2</sub> (93)	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CONHOH (96)
CH <sub>3</sub> CH=NO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	$\left\{ \begin{array}{l} \text{CH}_3\text{CHO (85)} \\ \text{CH}_3\text{CONHOH (2)}^b \end{array} \right\}$	CH <sub>3</sub> CONHOH (45)
CH <sub>3</sub> CH <sub>2</sub> CH=NO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	CH <sub>3</sub> CH <sub>2</sub> CHO (80) <sup>47</sup>	—
(CH <sub>3</sub> ) <sub>2</sub> C=NO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> C=O (84) <sup>47</sup>	—
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=NO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	$\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO (70)} \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CONHOH (4)}^b \end{array} \right\}$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CONHOH (28)
CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=NO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub> (81) <sup>229</sup>	

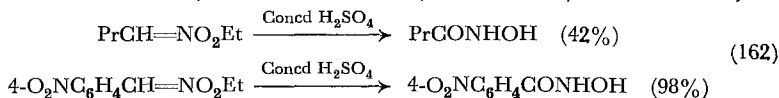
<sup>a</sup> With 10% H<sub>2</sub>SO<sub>4</sub>.<sup>b</sup> With 21% H<sub>2</sub>SO<sub>4</sub>.





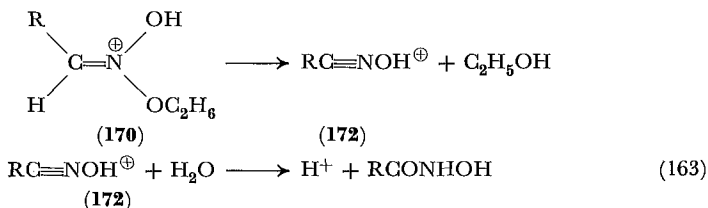
catalyzed hydrolysis of  $\alpha$ -ketonitronic esters to  $\alpha$ -ketonitroalkanes (equations 149–151) may be particular and proceed by a mechanism involving a protonated carbonyl group; formation of a resonance stabilized nitronate anion  $\left[ \begin{array}{c} \text{R}^1\text{C} - \text{C} - \text{N} - \text{O}^- \\ | \quad | \quad | \\ \text{O} \quad \text{R}^2 \quad \text{O} \end{array} \right]$ , also facilitates these reactions.

Hydroxamic acids are formed in concentrated sulfuric acid (31*N*) from both aliphatic and aromatic nitronic esters (equation 162); yields (higher with aromatics) are comparable to those obtained from nitronic acids (*via* nitronate salts) (Table 14)<sup>222</sup>. However, in



dilute (4*N*) sulfuric acid solution a difference in behavior is noted between nitronic esters and nitronic acids in forming hydroxamic acids. In the more dilute acid aliphatic nitronic acids form hydroxamic acids, but aromatic ones do not. The opposite is true of the nitronic esters. In 4*N* sulfuric acid solution aliphatic nitronic esters do not, but aromatic nitronic esters do form hydroxamic acids.

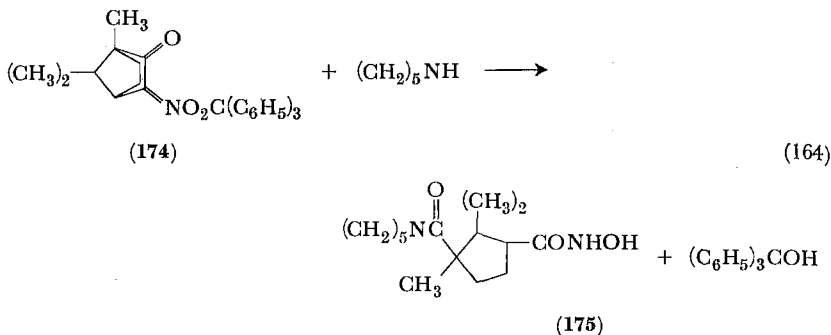
This difference in behavior between nitronic acids and esters in yet another acid-catalyzed reaction suggests, as in the 'ester Nef' reaction (equations 158–160), a mechanism which does not require a nitronic acid intermediate. In a nitrile oxide mechanism (see section III.C.1) the protonated ester **170** could lose alcohol, ultimately forming a protonated nitrile oxide **172**, which hydrates to the hydroxamic acid (equation 163). The formation, in 4*N* sulfuric acid, of more hydroxamic acid from aliphatic nitronic acids than



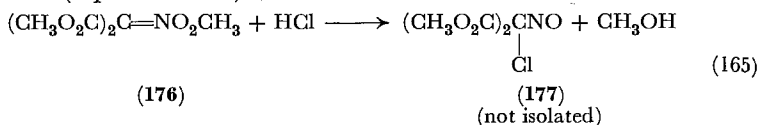
from aliphatic nitronic esters (which form aldehydes) is readily explained by assuming that **170** is more stable (forms nitrile oxide more slowly) than the corresponding intermediate,  $\text{RCH}=\overset{\oplus}{\text{N}}(\text{OH})_2$  (**173**), obtained from the acid. The assumed relatively greater stability of **170** over **173** also explains the observed formation of hydroxamic acids from aromatic nitronic esters, and the absence of

formation of hydroxamic acids from the corresponding aromatic nitronic acids (which tautomerize to nitroalkanes) under the same conditions in 4*N* sulfuric acid.

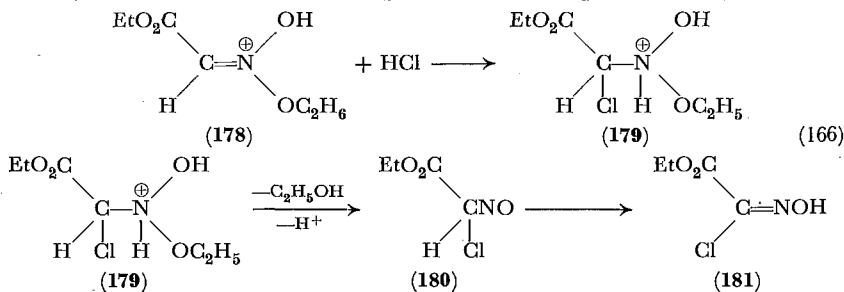
A hydroxamic acid **175** has been prepared from a nitronic ester (**174**) in a basic medium; a nitrile oxide intermediate has been postulated for this reaction<sup>414</sup> (equation 164).



Hydrogen chloride should add to nitronic esters—as it does to nitronic acids—to yield chloronitroso compounds or hydroxamic acid chlorides (section III.C.1a). Methyl dicarbomethoxymethane-nitronate (**176**) produces oxides of nitrogen and a blue color (possibly compound **177**; not isolated) when treated with aqueous hydrogen chloride<sup>394</sup> (equation 165).



The addition of hydrogen chloride to ethyl carbethoxymethane-nitronate leads to the hydroxamic acid chloride **181**. Addition probably proceeds, as with nitronic acids, through a protonated ester **178** and an HCl adduct **179** which loses ethanol to form a chloronitroso compound **180**. Rearrangement of **180** would yield the hydroxamic acid chloride product, **181** (equation 166).

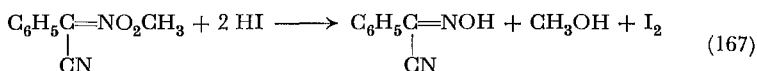


Since electrophilic additions to nitronic acids (section III.C.1b) appear to involve the nitronate anion in acid solution, no reactions of this type are to be expected for nitronic esters. None are found. Reactions of ethyl and methyl acetamidomethanenitronate with aqueous bromine are reported to produce 1-bromonitronic esters  $[H_2NCOC(Br)=NO_2R; R = CH_3, C_2H_5]$ , solids which decompose slowly at room temperature<sup>403</sup>. The possibility also exists, however, that these products are N-bromo derivatives,  $BrNHCOCCH=NO_2R$ .

## 2. Oxidation and reduction reactions of nitronic acid esters

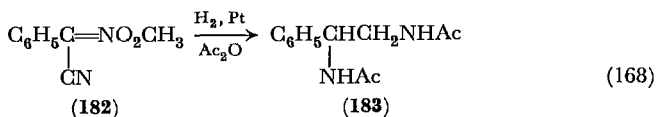
Nitronic esters, like nitronic acids, are good oxidizing agents. They are easily reduced to oximes. Only a few reducing agents have been employed in reactions with nitronic esters. Reaction of nitronic esters with added oxidizing agents apparently has not been studied.

Hydrogen iodide reduces nitronic esters to oximes with formation of iodine<sup>394,412</sup> (equation 167). The reaction may involve an addition

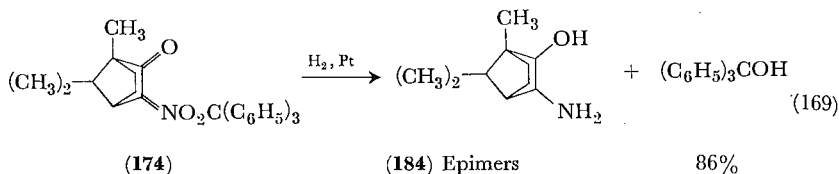


of hydrogen iodide, followed by loss of alcohol to yield a transient iodonitroso compound; reduction of this product by hydrogen iodide would yield the oxime. Unlike the reduction of nitronic acids with hydrogen iodide<sup>276</sup>, the reaction rate is quite variable and is not cleanly quantitative. Arndt and Rose<sup>394</sup> observed that when esters are treated with concentrated hydriodic acid, the number of equivalents of iodine formed, and the rate of reaction, varied with the structure of the ester: 4- $CH_3C_6H_4SO_2CH=NO_2CH_3$  reacted exothermically to liberate 2–2.5 equivalents of iodine;  $C_6H_5CH=NO_2CH_3$  reacted on warming to produce 0.5 equivalent, and  $(CH_3O_2C)_2C=NO_2CH_3$  produced 4.36–4.38 equivalents. No iodine was formed when 4- $BrC_6H_4CH=NO_2CH_3$  was treated with cold colorless azeotropic hydroiodic acid<sup>394</sup>.

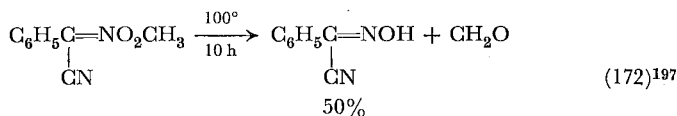
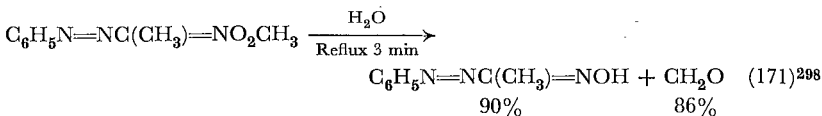
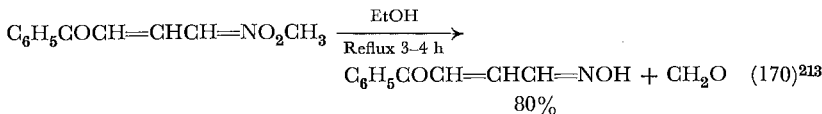
Although reduction of a nitronic acid to an amine appears not to have been described, nitronic esters have been so reduced. Methyl  $\alpha$ -cyanophenylmethanenitronate (**182**) is hydrogenated (platinum, acetic anhydride) completely to phenyl-1,2-diaminoethane, isolated as the bisacetyl derivative **183**<sup>411</sup> (equation 168).



Hydrogenation of keto ester **174** led to triphenyl carbinol and a mixture of epimeric amino alcohols **184**<sup>414</sup> (equation 169).

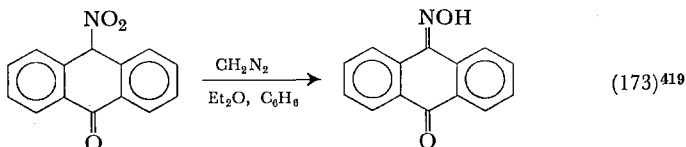


An auto-oxidation-reduction reaction of nitronic esters is one of their most important and characteristic properties. It is the disproportionation of the nitronic ester to form an oxime and an aldehyde or ketone (Table 15) and is of synthetic utility for preparing each of these products. The reaction proceeds by heating in solution in various solvents, or, in the absence of solvents (equations 170–172). It appears to have been discovered by Nef (1894)<sup>15,404</sup>. Yields,

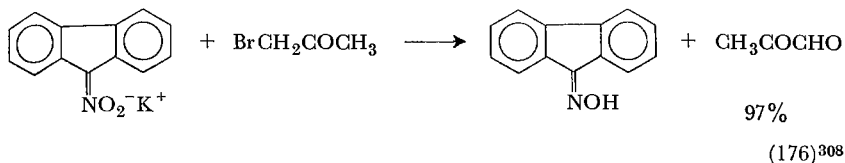
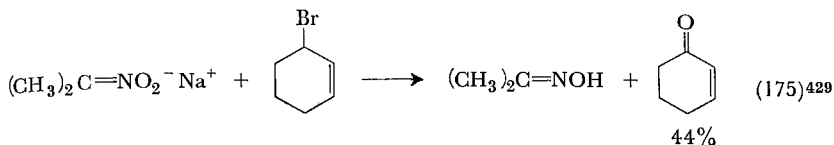
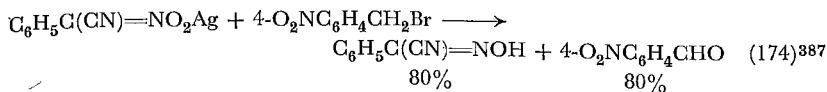


although seldom reported, generally appear to be very good.

The reaction is not limited to the few types of stable nitronic esters. It is also observed with esters generated *in situ*. Alkylations of nitronic acids or nitroalkanes with diazomethane, alkyl fluoroborates, or alkyl halides can produce oximes. The synthetic value of the reaction applied to simple esters (methyl, ethyl) lies in oxime synthesis (e.g. equation 173)<sup>419</sup>; cf. Table 15 for other examples.





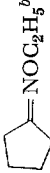

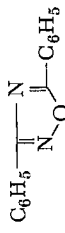

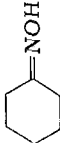
Preparation of aldehydes and ketones from nitronic esters generated *in situ* is important synthetically<sup>392,393,409,450</sup>. An alkali or silver nitronate reacts with a primary or secondary alkyl halide in a solvent such as ethanol, usually at reflux temperature (equations 174–176).


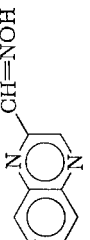
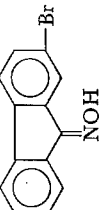


It is possible to examine the scope of this reaction since many examples are known (Table 16). The reaction has been developed as a synthetic method<sup>392,393,450</sup>. The customary procedure involves preparation of a nitronate salt from the nitroalkane and sodium ethoxide in ethanol, followed by addition of the halide. A short period of heating under reflux (1–3 h) is usually sufficient to complete the reaction. Yields of both carbonyl compound and oxime are usually excellent. Side reactions seem to present no difficulties and are seldom encountered. The range of structural variations allowed in nitro compound and halide is quite large. Primary and secondary nitroalkanes seem equally effective. Yields of aldehydes (from primary halides) appear to equal those of ketones from secondary halides. Aliphatic, alicyclic, and arylalkyl halides and nitronate salts have been employed with equal success. The method has been employed successfully in the synthesis of 1,2-dicarbonyl compounds from  $\alpha$ -halo ketones<sup>308,450</sup>. Although alkali metal salts have been employed in most studies, silver salts are equally effective<sup>15,387,417</sup>. What appears to be the first example of the reaction, due to Nef<sup>15</sup>, employed silver 1-nitroethanenitronate and ethyl iodide to yield acetaldehyde and  $\alpha$ -nitroacetaldoxime.

The mechanism of the disproportionation of nitronic esters to carbonyl compounds has been studied<sup>421a</sup>. Generally, the reaction

TABLE 15. Decomposition of nitronic esters.

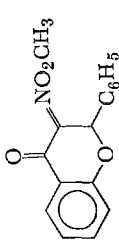
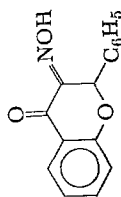
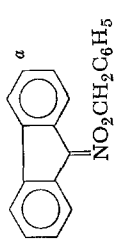
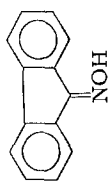
Nitronic ester	Solvent, Temp., (°C)	Products	Yield (%)	Ref.
$\text{H}_2\text{NCOC}(\text{CN})=\text{NO}_2\text{C}_6\text{H}_5$	$\text{H}_2\text{O}$ , heat	$\text{H}_2\text{NCOC}(\text{CN})=\text{NOH}$ $\text{CH}_3\text{CHO}$	—	15, 405, 406
$\text{C}_6\text{H}_5\text{O}_2\text{CCH}=\text{NO}_2\text{CH}_3$	none, 65°	$\text{C}_6\text{H}_5\text{O}_2\text{CCH}=\text{NOH}$ $\text{CH}_2\text{O}$	—	394
$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{C}_2\text{H}_5^a$	$\text{H}_2\text{O}$ , 60–70°	$(\text{CH}_3)_2\text{C}=\text{NOH}$ $\text{CH}_3\text{CHO}$	20	390
	$\text{H}_2\text{O}$ , 60–70°		86	390
			5	
$4\text{-BrC}_6\text{H}_4\text{CH}=\text{NO}_2\text{CH}_3$	none, 80°	$\text{CH}_3\text{CHO}$ $4\text{-BrC}_6\text{H}_4\text{CH}=\text{NOH}$ $\text{CH}_2\text{O}$	—	394
	15% $\text{HCl}$ , 100°		—	394
$\text{C}_6\text{H}_5\text{CH}=\text{NO}_2\text{CH}_3$	none, 25–100°	$4\text{-BrC}_6\text{H}_4\text{CO}_2\text{H}$ $\text{C}_6\text{H}_5\text{CHO}$ $\text{CH}_2\text{O}$	—	394
	15% $\text{HCl}$ , 100°		—	394 •
	$\text{H}_2\text{O}$ , 50–60°		51–79	390

				7-19
CH <sub>3</sub> CHO				
2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> C(CH <sub>3</sub> )=NOH	H <sub>2</sub> O, 100°			229
CH <sub>2</sub> O				
2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> C(CH <sub>3</sub> )=NOH	H <sub>2</sub> O, 100°			299
CH <sub>2</sub> O				
4-BrC <sub>6</sub> H <sub>4</sub> -N=N-C <sub>6</sub> H <sub>4</sub> -Br-4	none, 25°			23
CH <sub>3</sub> CHO				
4-ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> C(CH <sub>3</sub> )=NOH	H <sub>2</sub> O, 100°			298
CH <sub>2</sub> O				
	none, 120-140°			420
C <sub>6</sub> H <sub>5</sub> C(CN)=CHCH=NOH	toluene, 110°			191
CH <sub>2</sub> O				
4-BrC <sub>6</sub> H <sub>4</sub> COCH=CHCH=NOH	EtOH, 80°			213
CH <sub>2</sub> O				
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCH=CHCH=NOH	EtOH, 80°			213
CH <sub>2</sub> O				
	EtOH, warm			204

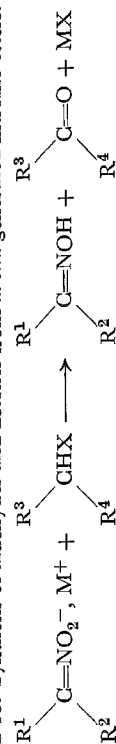
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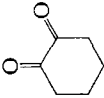
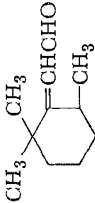


TABLE 15—continued

Nitronic ester	Solvent, Temp., (°C)	Products	Yield (%)	Ref.
$C_6H_5C(CN)=NO_2CH_2C_6H_5$	none, 25°	$CH_2O$ $C_6H_5C(CN)=NOH$ $C_6H_5CHO$	— — —	411
	none, 100°		25	344
$CH=NO_2CH_3$   $C=NNHC_6H_5$   $CH=NNHC_6H_5$	none, 120–130°	$CH_2O$ $CH=NOH$   $C=NNHC_6H_5$   $CH=NNHC_6H_5$ $CH_2O$	— — —	420
	EtOH, 80°	 $C_6H_5CHO$	87	84


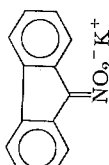
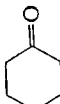
<sup>a</sup> Formed *in situ*.<sup>b</sup> Formed *in situ* from sodium nitronates and  $(EtO)_3BF_4^-$ . The O-alkyl oxime products are believed to result from the alkylating agent present.

TABLE 16. Synthesis of aldehydes and ketones from *in situ* generated nitronic esters.

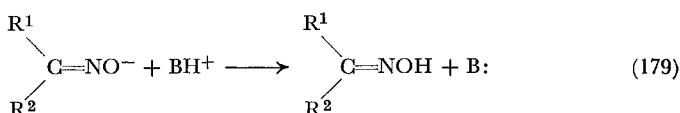
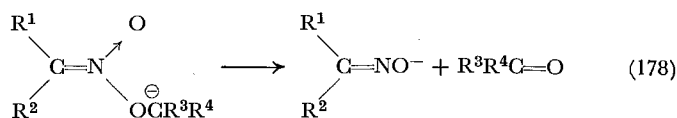
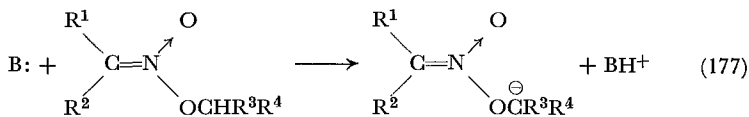
Nitronate salt $\text{R}^1\text{R}^2\text{C}=\text{NO}_2^-, \text{M}^+$	Alkyl halide $\text{R}^3\text{R}^4\text{CHX}; \text{X} =$	Aldehyde or ketone, $\text{R}^3\text{R}^4\text{C}=\text{O}$	Yield (%)	Ref.
$(\text{CH}_3)_2\text{C}=\text{NO}_2^-\text{Na}^+$	Br	$\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CHCHO}$	54	392
	Cl			
	Br	$4\text{-BrC}_6\text{H}_4\text{CHO}$	30	450
	Cl	$\text{C}_6\text{H}_5\text{CHO}$	70	5, 388, 393
	Br	$4\text{-F}_3\text{CC}_6\text{H}_4\text{CHO}$	73	5, 388, 393, 450
	Br	$4\text{-NCC}_6\text{H}_4\text{CHO}$	77	5, 388, 393
	Br	$4\text{-CH}_3\text{C}_6\text{H}_4\text{CHO}$	70	5, 388, 393
	Br	$4\text{-CH}_3\text{O}_2\text{CC}_6\text{H}_4\text{CHO}$	72	5, 388
	Br	$3,4\text{-(CH}_2\text{O}_2)_2\text{C}_6\text{H}_3\text{CH}_2\text{COCH}_3$	90	450
	Br	$\text{OHCC}(\text{CH}_3)=\text{CHC}\equiv\text{CCH}=\text{C}(\text{CH}_3)\text{CHO}$	61	392
	I	$4\text{-I}(\text{CH}_3)_2\text{N}^+\text{I}^-\text{C}_6\text{H}_4\text{CHO}$	68	5, 388
	Br	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$	75	392
	Br		80	392

(continued)

Table 16—continued

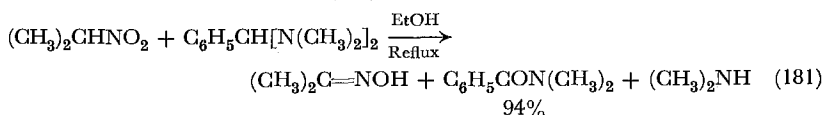
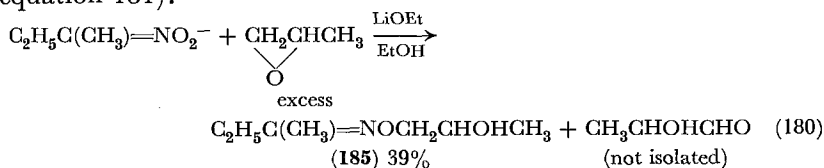
Nitronate salt $R^1R^2C=NO_2^-, M^+$	Alkyl halide $R^3R^4CHX; X =$	Aldehyde or ketone, $R^5R^6C=O$	Yield (%)	Ref.
	Br	$n-C_9H_{19}CHO$	46	450
	Br	$(CH_3)_2C=C(CH_3)CH_2CH_2C(CH_3)=CHCHO$	—	392
	Br	$n-C_{10}H_{21}CHO$	85	450
	Br	$CH_3COC(CH_3)=CHC\equiv CCH=C(CH_3)COCH_3$	56	392
	Br	$(CH_3)_2C=CHCH_2CH_2C(CH_3)=CHCH_2CH_2C(CH_3)=CHCHO$	—	392
	Cl	$C_6H_5CHO$	69	389
$C_6H_5CH=NO_2^-, Na^+$	Cl	$C_6H_5CHO$	77	387
	Cl	$4-NC_6H_4CHO$	—	387
	Cl	$2,4-(CH_3O)_2C_6H_3CHO$	—	387
$C_6H_5C(CN)=NO_2^-, Ag^+$	Br	$(C_6H_5)_2C=O$	(Very good)	417
$C_6H_5C(CN)=NO_2^-, Na^+$	Cl	$C_6H_5CHO$	—	387
	I	$CH_2O$	—	84
	Br	$CH_3CHO$	—	84
	Br	$CH_3COCHO$	97	308
	Br, I	$(CH_3)_2C=O$	—	84
	Cl	$C_2H_5O_2CCHO$	—	84
	Br		—	84
	Br	$(C_2H_5O_2)_2C=O$	—	84
	Br	$C_6H_5COCHO$	84	308

appears to proceed more rapidly, and in higher yield, in a solvent than without a solvent. A slightly basic medium (pH 7–9) favors the reaction. A strongly basic medium is avoided to minimize self-condensation of the aldehyde or ketone products. Heating a nitronic ester with acids leads to a different reaction, formation of an alcohol rather than aldehydes or ketones (section IV.C.1). These observations agree with a mechanism, suggested by Kornblum, involving base attack at the  $\alpha$ -carbon of the alkyl group<sup>23</sup> (equations 177–179).



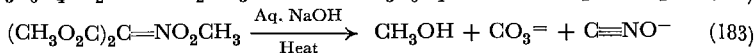
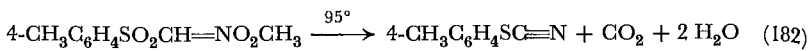
However, the rate of decomposition of alkyl 3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadiene nitronates is not base-catalyzed, and a cyclic intramolecular decomposition mechanism has been suggested.<sup>421a</sup>

Variations of the nitronic ester disproportionation reaction can lead to products other than aldehydes, ketones, and oximes. Epoxides react with nitronates (lithium ethoxide catalyst) to produce oxime ethers (e.g. **185**) when an excess of epoxide is employed; the expected  $\alpha$ -hydroxy aldehydes were not isolated<sup>451</sup> (equation 180). Amides have been prepared by reaction of nitroalkanes with amines<sup>450</sup> (equation 181).

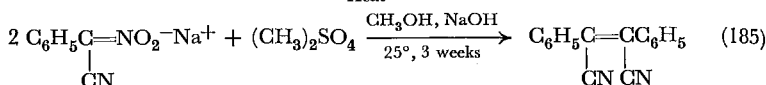
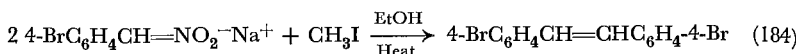


Heating methyl 4-toluenesulfonylmethanenitronate produces 4-tolyl thiocyanate and carbon dioxide, but no formaldehyde<sup>394</sup> (equation

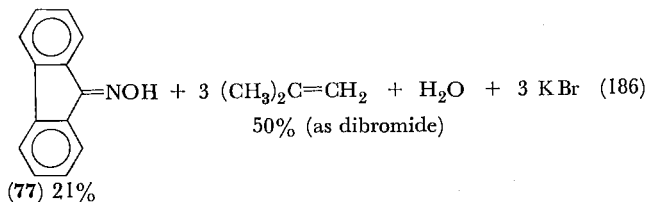
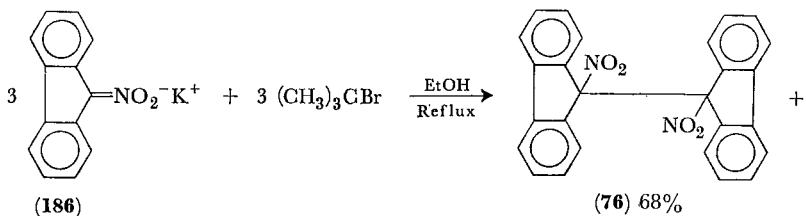
182). Heating methyl dicarbomethoxymethanenitronate with aqueous sodium hydroxide produced methanol, carbonate, and fulminate (isolated as the silver salt)<sup>394</sup> (equation 183)



The formation of stilbenes from what appear to be *in situ*-generated nitronic esters has been observed<sup>84,411</sup> (equations 184, 185).

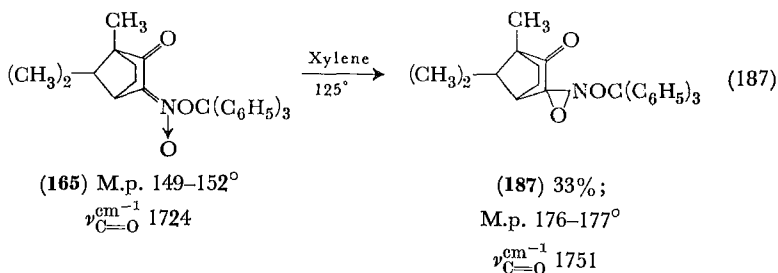


Nitronic esters of tertiary alcohols cannot disproportionate to form aldehydes or ketones. Such nitronic esters are reported to form *in situ* in hot ethanol solution from potassium fluorene-9-nitronate (**186**) and tertiary bromides (*t*-butyl bromide, 2-bromo-2-phenylpropane, and triphenylchloromethane)<sup>84,205</sup>. These esters were not isolated. The products actually isolated are the same as those derived from fluorene-9-nitronic acid (see section III.C.2), namely fluorone oxime (**77**) and the 1,2-dinitroethane **76** (equation 186). When *t*-butyl bromide was a reactant, isobutylene was isolated as the dibromide.

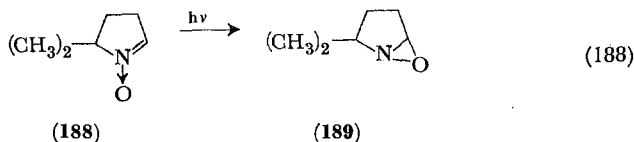


Keto ester **165** is isomerized by heating at 125° in xylene to form oxaziran **187** in the first example of such a conversion into this valence bond isomer of a nitronic ester<sup>414,452</sup> (equation 187). The

conjugated carbonyl band of the nitronic ester at  $1724\text{ cm}^{-1}$  is



shifted to  $1751\text{ cm}^{-1}$  by the rearrangement. The extent to which oxaziran intermediates are involved in nitronic acid and ester chemistry is yet to be determined<sup>453</sup>. The conversion of the related nitrones into oxazirans is known; e.g. **188**  $\rightarrow$  **189**<sup>21, 24, 454, 455</sup> (equation 188).



### 3. 1,3-Dipolar addition reactions of nitronic acid esters

Nitronic esters undergo 1,3-dipolar addition to olefins, a reaction discovered<sup>456</sup> and developed by Tartakovskii and co-workers<sup>398, 400, 436, 456--458</sup>. The products are stable, often crystalline, 2-alkoxyisoxazolidines (Table 17). A wide variety of olefins have been added to methyl dinitromethanenitronate (**190**). The reactions are conducted under mild conditions—room temperature in methylene chloride or without solvent. Yields are good to excellent in most examples (equations 189, 190; Table 17).

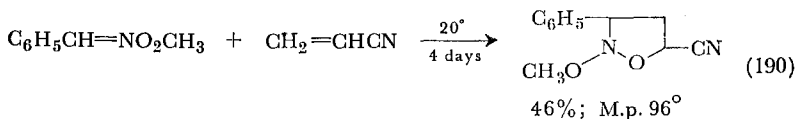
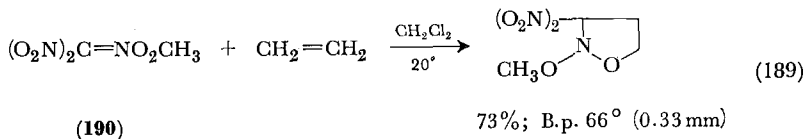
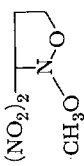
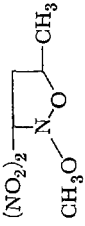
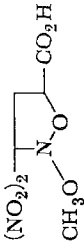
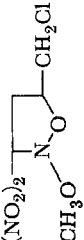
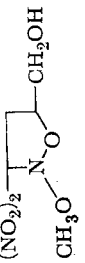
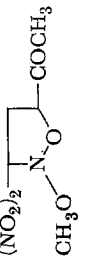
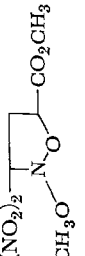




TABLE 17. 1,3-Dipolar additions of nitronic acid esters to olefins.  
 Synthesis of isoxazolidines

Nitronic ester	Olefin	Product	Yield (%)	Ref.
$(\text{NO}_2)_2\text{C}=\text{NO}_2\text{CH}_3^a$	$\text{CH}_2=\text{CH}_2$		73	398
	$\text{CH}_2=\text{CHCH}_3$		68	398
	$\text{CH}_2=\text{CHCO}_2\text{H}$		91	398
	$\text{CH}_2=\text{CHCH}_2\text{Cl}$		81	398, 456
	$\text{CH}_2=\text{CHCH}_2\text{OH}$		91	398
	$\text{CH}_2=\text{CHCOCH}_3$		88	398
	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$		27	398, 456

$\text{CH}_2=\text{CHOCOCCH}_3$	93	398
	76	398
$(\text{NO}_2)_2\text{C}=\text{NO}_2\text{CH}_3^a$	20	398
$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	63	398
$\text{CH}_2=\text{CHC}_6\text{H}_5$	65	400
$\text{O}_2\text{NCH}=\text{NO}_2\text{CH}_3^a$	—	423
$(\text{NO}_2)_2\text{C}=\text{NO}_2\text{CH}_2\text{CH}_2\text{I}^a$	—	423
	—	456
$\text{CH}_2=\text{CH}_2$	—	456

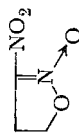
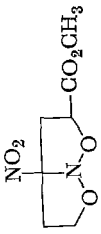

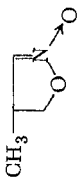
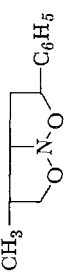
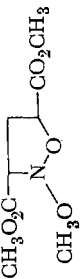
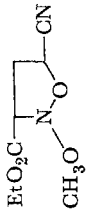
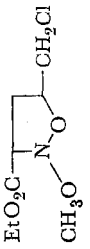
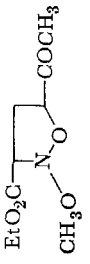
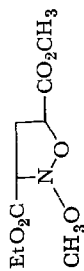
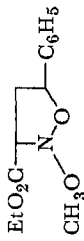

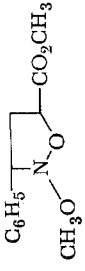
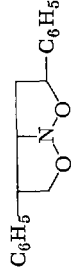
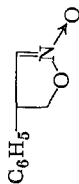




TABLE 17—continued

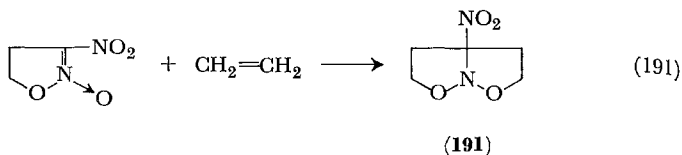
Nitronic ester	Olefin	Product	Yield (%)	Ref.
	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$		—	456
$(\text{NO}_2)_2\text{C}=\text{NO}_2\text{C}_6\text{H}_5^a$	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$		38	398
	$\text{CH}_2=\text{CHC}_6\text{H}_5$		—	456
$\text{CH}_3\text{O}_2\text{CCH}=\text{NO}_2\text{CH}_3$	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$		74	458
$\text{EtO}_2\text{CCH}=\text{NO}_2\text{CH}_3$	$\text{CH}_2=\text{CHCN}$		76	458
	$\text{CH}_2=\text{CHCH}_2\text{Cl}$		75	458
	$\text{CH}_2=\text{CHCOCH}_3$		78	458

$\text{CH}_2=\text{CHCO}_2\text{CH}_3$		90	458
$\text{CH}_2=\text{CHC}_6\text{H}_5$		64	458
$\text{C}_6\text{H}_5\text{CH}=\text{CHNO}_2\text{CH}_3$		46	456, 457
$\text{CH}_2=\text{CHCO}_2\text{CH}_3$		34	457
$\text{CH}_2=\text{CHC}_6\text{H}_5$		—	456

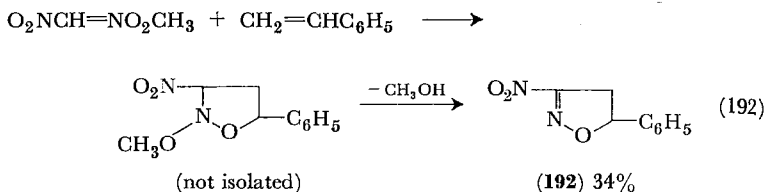


<sup>a</sup> Prepared *in situ*.

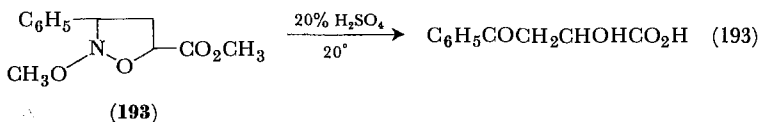
The reaction has been extended to cyclic nitronic esters as in the preparation of bicyclic **191**<sup>436,456,458a</sup> (equation 191).



The scope of the reaction appears large, but has not been completely defined since relatively few nitronic esters have been employed. The required nitronic esters, some of which are very unstable (e.g. **190**), may be generated conveniently *in situ*. Thus, the reaction is not limited to the few stable nitronic esters. The reaction has failed in certain reported instances. The reaction of methyl phenylmethanenitronate with styrene failed to yield an isoxazolidine<sup>457</sup>. 2-Alkoxyisoxazolidine products having a hydrogen in the 3-position may eliminate alcohol to form a 2-isoxazoline; for example, in the reaction of methyl nitromethanenitronate with styrene the product was **192**<sup>400</sup> (equation 192).

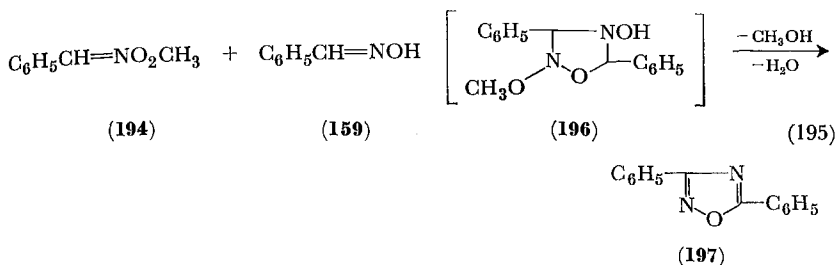
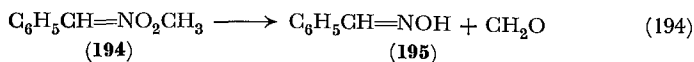


The structure of the adducts derived from unsymmetrical olefins has been established in a few instances<sup>398,400,457</sup>. Vinyl compounds ( $\text{CH}_2=\text{CHR}$ ) examined thus far add so that the R group appears in the 5-position. Hydrolysis of **193** with dilute sulfuric acid led to  $\beta$ -benzoylacetic acid, thereby establishing the 3,5-relationship of phenyl and carbomethoxy<sup>457</sup> (equation 193).

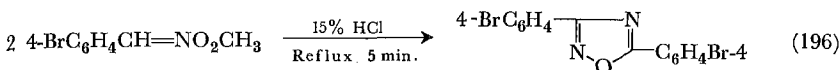


The addition of methyl phenylmethanenitronate (**194**) to benzald-oxime (**195**) led readily to 3,5-diphenyl-1,2,4-oxadiazole (**197**), which is also formed slowly from **194** on standing<sup>457</sup>. Since oximes form readily from nitronic esters (equation 194), the formation of

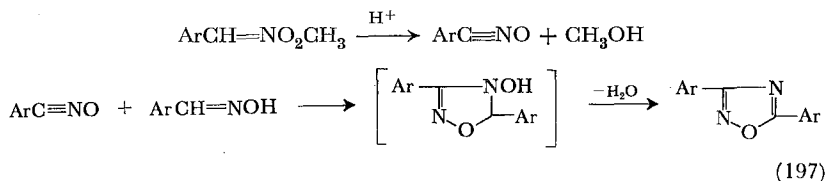
oxadiazoles from certain nitronic esters on standing<sup>23,457</sup> appears to be simply an addition of product to reactant. The intermediate **196** demethanolates and dehydrates to yield the oxadiazole **197** (equation 195)



The demethanolation of a 2-methoxyisoxazolidine has been shown to be acid-catalyzed<sup>400</sup>, thus offering an explanation for the observed facile conversion of nitronic esters into oxadiazoles in hot hydrochloric acid<sup>394</sup> (equation 196). An alternate acid-catalyzed



mechanism could involve formation of a nitrile oxide intermediate from the nitronic ester (see section III.C.1.a), followed by addition of the oxime<sup>400</sup>. Diene addition of nitrile oxides to olefins has been reported<sup>457,459</sup> (equation 197).



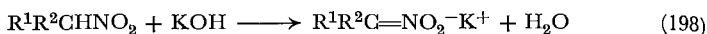
## V. NITRONIC ACID DERIVATIVES OTHER THAN ESTERS

### A. Nitronic Acid Salts

Salts of nitronic acids may be prepared by reaction of bases with nitronic acids. However, they are usually most readily prepared from nitroalkanes, employing a suitable solvent. Unlike most nitroalkanes, nitronic acids are soluble in sodium bicarbonate solution.

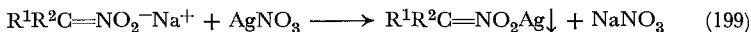
Many nitronate salts are shock sensitive explosives, and are particularly hazardous when anhydrous. The alkali metal salts are useful for purifying and isolating nitronic acids and nitroalkanes<sup>1</sup>. Properties of salts of polynitroalkanes have been reviewed<sup>460</sup>.

Several metal cations have been employed in the preparation of nitronate salts. The sodium and potassium salts are the most common<sup>32,198</sup>; these are prepared by treatment of a nitroalkane with aqueous sodium or potassium hydroxide, or the ethanolic metal ethoxides (equation 198).

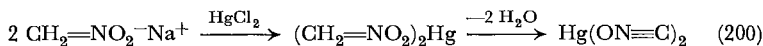


The usually colorless mononitronate salts often precipitate from cold solutions and may be isolated by filtration<sup>339</sup>. Alkali metal salts of 1,1-dinitroalkanes are yellow and often less soluble than mononitronates<sup>194</sup>. The potassium salts are less soluble than sodium salts.

Several heavy metal salts are known, the most common being silver, mercury, and copper<sup>1,198,229,461-464</sup>. These insoluble, largely covalent compounds may be prepared from the alkali salts by metathesis (equation 199)

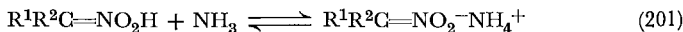


The silver salts are employed for nitronic ester synthesis (Table 11, method B, in section IV.A.1). The silver salt of nitroform exists in colorless and yellow modifications suggesting the possibility of CAg and OAg forms<sup>147,415</sup>. Insoluble mercury methanenitronate decomposes to form mercury fulminate<sup>15,462</sup> (equation 200).



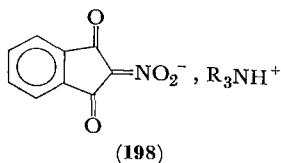
The qualitative test for nitronic acids employs aqueous ferric chloride. The resulting characteristic red-brown color<sup>1,159</sup> is probably that of a ferric salt,  $(FeO_2N=CR^1R^2)^{++}$ ; cf. section VI.

Nitronate salts of weak bases such as ammonia and amines may be prepared from nitronic acids<sup>177</sup>. The reaction is conveniently conducted in ether solvent in which the salts are insoluble. On standing, the ammonium salts of weak nitronic acids liberate ammonia to regenerate the nitronic acid<sup>32,177</sup> (equation 201).



Nitroalkanes react directly with ammonia or amines<sup>366,465</sup>. The kinetics of this second-order process has been examined with

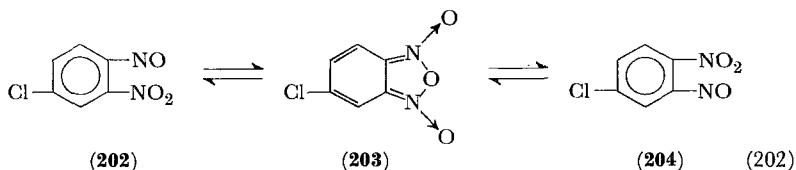
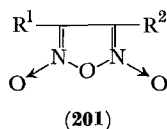
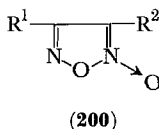
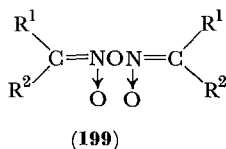
nitroethane<sup>112</sup>. 2-Nitro-1,3-indanedione readily forms stable salts **(198)** useful for characterization of amines<sup>366</sup>.



Nitronate salts are very useful and important reaction intermediates. They are employed in numerous reactions, either in solution or in suspension in anhydrous solvents. Typical are aldol-type condensation (Henry reaction), Michael addition, acylation, O- and C-alkylation, and halogenation (to form  $\alpha$ -halonitroalkanes). Thermal decomposition of nitronate salts has been studied<sup>422</sup>.

### B. Nitronic Acid Anhydrides

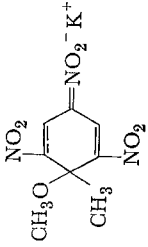
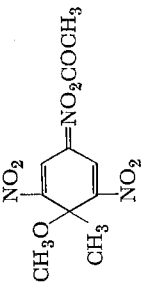
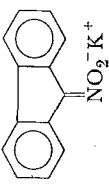
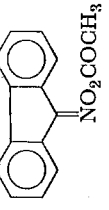
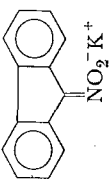
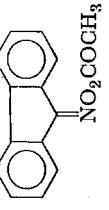
Simple nitronic anhydrides—acyclic **199** or cyclic **201**—appear to be unstable compounds. The cyclic anhydrides **201** are known as furazan dioxides. Attempts to prepare them by oxidation of furazan oxides **(200)** have failed<sup>466–468</sup>. Evidence for a cyclic nitronic acid



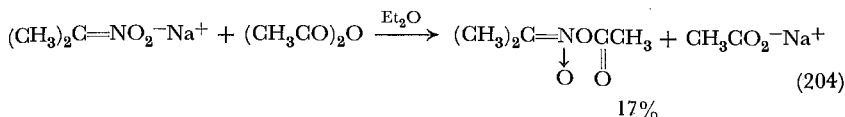
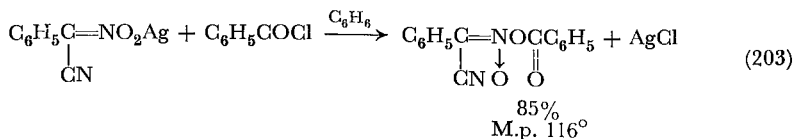
anhydride **203** as a reaction intermediate is found in the facile interconversion of 4- and 5-chloro-2-nitronitrosobenzenes (**202** and **204**, respectively) (equation 202). Heating pure samples of either **202** or **204** at low concentration in refluxing tetrachloroethane gave a mixture of equal parts of the two isomers, regardless of the direction from which equilibrium was approached<sup>466</sup>.

The known stable nitronic acid anhydrides are mixed anhydrides derived from *secondary* nitronic acids (with one exception) and carboxylic acids. These nitronic carboxylic acid anhydrides (Table 18) appear to be somewhat more stable than most nitronic esters.

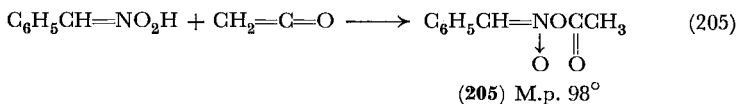
TABLE 18. Synthesis of nitronic carboxylic acid anhydrides.

Nitro compound	Acylation agent	Anhydride	Yield (%)	Ref.
$(\text{CH}_3)_2\text{C}=\text{NO}_2^-\text{Na}^+$	$(\text{CH}_3\text{CO})_2\text{O}$	$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{COCH}_3$	17	470
$(\text{CH}_3)_2\text{CHNO}_2$	$(\text{C}_2\text{H}_5\text{CO})_2\text{O}$	$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{COC}_2\text{H}_5$	6	470
	$(\text{CH}_3\text{CO})_2\text{O}$ , $\text{CH}_3\text{CO}_2^-\text{K}^+$	$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{COCH}_3$	8	470
$\text{C}_6\text{H}_5\text{CH}=\text{NO}_2\text{H}$	$(\text{C}_2\text{H}_5\text{CO})_2\text{O}$ , $\text{C}_2\text{H}_5\text{CO}_2^-\text{K}^+$	$(\text{CH}_3)_2\text{C}=\text{NO}_2\text{COC}_2\text{H}_5$	10	470
$\text{C}_6\text{H}_5\text{C}(\text{CN})=\text{NO}_2\text{Ag}$	$\text{CH}_2=\text{C}=\text{O}$	$\text{C}_6\text{H}_5\text{CH}=\text{NO}_2\text{COCH}_3$	—	275
	$\text{C}_6\text{H}_5\text{COCl}$	$\text{C}_6\text{H}_5\text{C}(\text{CN})=\text{NO}_2\text{COC}_6\text{H}_5$	85	411, 433
$\text{C}_6\text{H}_5\text{C}(\text{CN})=\text{NO}_2^-\text{Na}^+$	$\text{C}_6\text{H}_5\text{COCl}$	$\text{C}_6\text{H}_5\text{C}(\text{CN})=\text{NO}_2\text{COC}_6\text{H}_5$	—	411
	$\text{CH}_3\text{COCl}$		—	170
	$\text{CH}_3\text{COCl}$		—	275
	$\text{C}_6\text{H}_5\text{COCl}$		—	275

They may be prepared by acylation of a secondary nitronate salt with an acid chloride, or anhydride<sup>275, 411, 469-471</sup>. Silver and alkali metal salts have been used (equations 203, 204).



The nitronate salt does not need to be prepared first. Treatment of a secondary nitroalkane with potassium acetate and an acid anhydride leads to a low yield of mixed anhydride<sup>470</sup>. Ketene may be used as in the preparation of **205**, the only known anhydride derived from a primary nitronic acid<sup>275, 471</sup> (equation 205). This compound could not be prepared by reaction of sodium phenylmethanenitronate with acetyl chloride<sup>470</sup>.



The physical properties of nitronic carboxylic anhydrides have not been examined extensively. No spectra appear to have been recorded. The compounds which have been prepared (Table 18) are relatively stable, distillable liquids or crystalline solids.

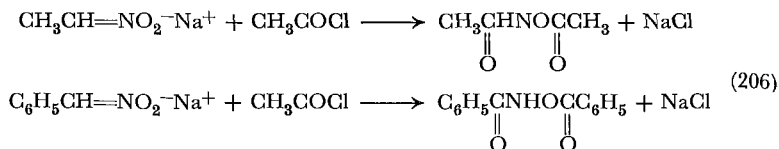
Studies of reactions of nitronic carboxylic anhydrides are few. From what is known their reactions appear comparable to those of carboxylic anhydrides. However, a simple hydrolytic cleavage reaction to carboxylic and nitronic acids (or nitroalkanes) is not always found.

Two reaction patterns are distinguished. Anhydrides derived from *primary* nitronic acids rearrange with great ease to hydroxamic acid esters. Those derived from *secondary* nitronic acids cannot undergo this rearrangement, but form other products.

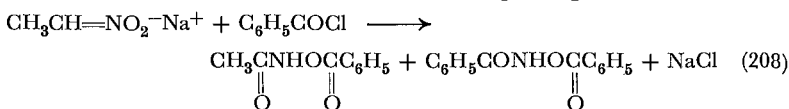
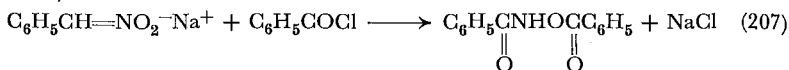
Reactions of primary nitronic carboxylic anhydrides prepared *in situ* can be observed by examining the reaction of salts of primary nitroalkanes with acid chlorides and anhydrides (equation 206). Nitronic carboxylic anhydrides have not been isolated from these reactions. Hydroxamic acid esters are the principal products<sup>471-475</sup>.



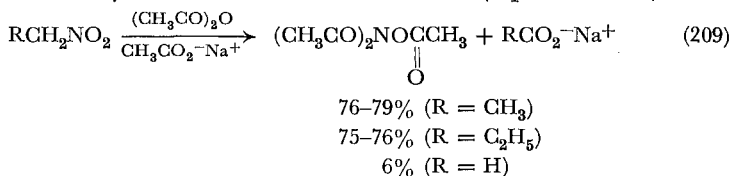
The reaction was discovered by Kissel in 1882<sup>472</sup>. Both sodium



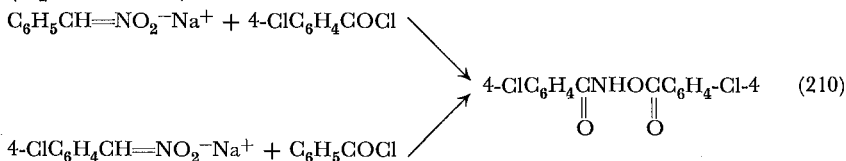
ethanenitronate and sodium phenylmethanenitronate can yield dibenzohydroxamic acid with benzoyl chloride<sup>62,472-475</sup> (equations 207, 208).



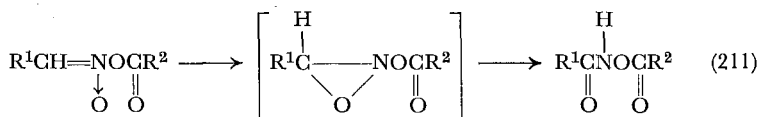
When primary nitronate salts are treated with an excess of acylating agent, trisacylhydroxylamines result<sup>245</sup>. Acylation and transacylation of the hydroxamic ester are involved (equation 209).



Van Raalte observed that acyl exchange can occur when different aryl groups are present in the acid chloride and nitronate salt<sup>62</sup> (equation 210).

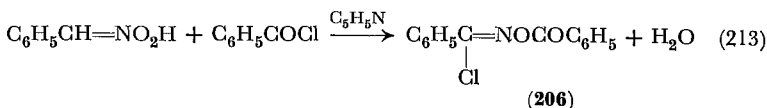
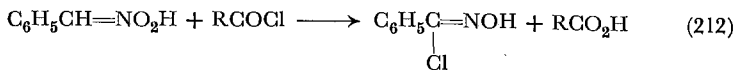


The mechanism of hydroxamic ester formation as suggested originally by Nef<sup>473</sup> probably involves initial formation of a nitronic carboxylic acid anhydride followed by a tautomeric rearrangement (equation 211). An oxaziran intermediate is possibly involved. The thermal rearrangement of oxazirans to amides has been studied<sup>476</sup>

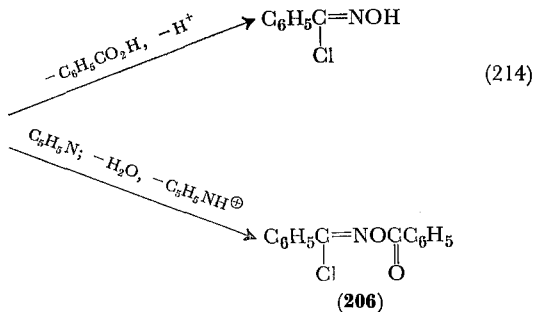
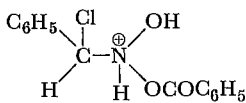
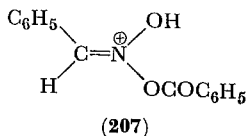


and is accelerated (relative to *N*-alkyl) by *N*-aryl substitution<sup>477</sup>. However, the actual conversion of a primary nitronic carboxylic anhydride into its isomeric hydroxamic ester has yet to be described.

Reactions of primary nitronic carboxylic anhydrides, prepared *in situ*, can also be examined by studying the reactions of primary nitronic acids, rather than the salts, with acid chlorides and anhydrides. Reaction of phenylmethanenitronic acid with acetyl or benzoyl chloride (or hydrogen chloride) leads to hydroxamic acid chloride **58**<sup>249, 275</sup> (equation 212). In the presence of pyridine one obtains the benzoyl derivative **206**, which is also obtained from **58** under the same conditions<sup>478</sup> (equation 213).

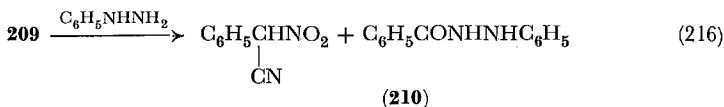
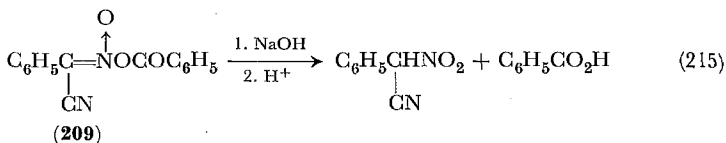


The mechanism of this reaction may parallel the hydroxamic acid chloride forming reactions of nitronic acids (section III.C.1.a) and esters (section IV.C.1). Addition of hydrogen chloride to protonated anhydride **207**, followed by loss of water and a proton from adduct **208** would yield **206**; loss of benzoic acid would yield **58** (equation 214).

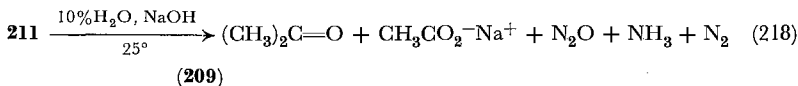
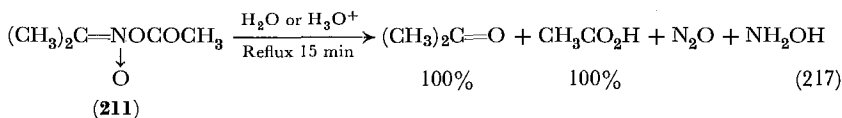


Reactions of secondary nitronic carboxylic acid anhydrides can be examined readily because of the stability of these substances. The acyl function remains intact in reaction products. The nitronic acid function may be destroyed, however.

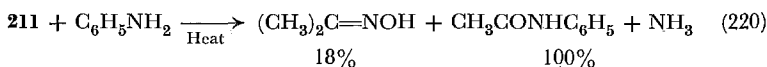
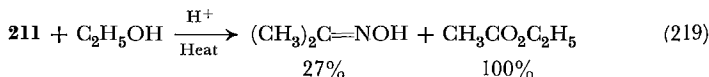
Hydrolysis of anhydride **209** with aqueous sodium hydroxide led to benzoic acid and  $\alpha$ -cyanophenylnitromethane; reaction with phenylhydrazine led to hydrazide **210** (equations 215, 216)<sup>411</sup>.



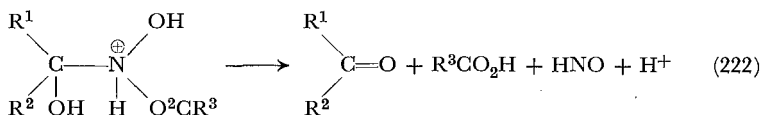
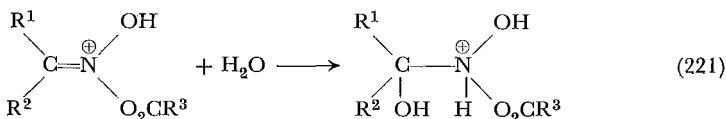
Hydrolysis of propane-2-nitronic acetic anhydride (**211**) by boiling water, with or without an acid catalyst, gave equal amounts of acetone and acetic acid in quantitative yield; nitrogen appeared as nitrous oxide and hydroxylamine (equation 217)<sup>470</sup>. In sodium hydroxide, hydrolysis of **211** occurred to give the same carbon products; nitrogen appeared as ammonia, nitrogen, and nitrous oxide, but no hydroxylamine was found (equation 218)<sup>470</sup>.



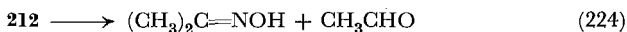
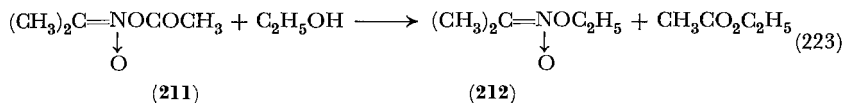
Ethanolysis of **211** in the presence of an acid catalyst, but not in ethanol alone, occurred to yield acetoxime, ethyl acetate, and a trace of acetone (equation 219)<sup>470</sup>. Aminolysis of **211** with aniline led to acetanilide (quantitative yield) as well as acetoxime and ammonia (equation 220)<sup>470</sup>.



The solvolysis reactions of nitronic carboxylic anhydrides would appear to require more than one mechanism. A simple cleavage to nitronic and carboxylic acids and derivatives (esters, salts) would explain most of the reactions. Alternative mechanisms may be involved, however. For example, acid-catalyzed hydrolysis of propane-2-nitronic anhydride (**211**) (equation 217) to yield acetone and nitrous oxide could be the result of Nef hydrolysis of the resulting propane-2-nitronic acid. However, as in the acid-catalyzed hydrolysis of nitronic esters to Nef products, the failure to isolate any nitroalkane (equation 217) as a product suggests an alternate mechanism. Like the 'ester-Nef' (section IV.C.1), an 'anhydride-Nef' is possible (equations 221, 222).



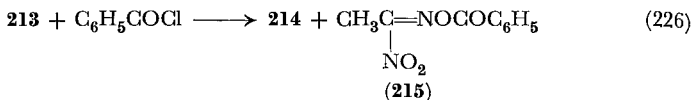
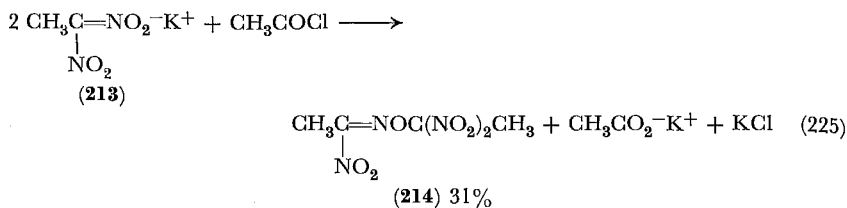
The formation of acetoxime and ethyl acetate from anhydride **211** by acid-catalyzed ethanolysis (equation 219) could be a result of nitronic ester formation (**212**), followed by disproportionation to the oxime (equations 223, 224),



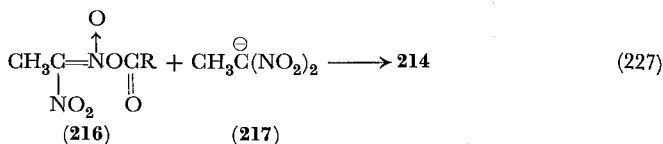
The base-catalyzed cleavage of anhydride **209** to  $\alpha$ -cyanophenyl-nitromethane and benzoic acid (equation 215) appears as a simple cleavage to nitronate anion followed by tautomerization to the nitro compound. On the other hand, the base-catalyzed cleavage of anhydride **211** (equation 218) to acetone and ammonia, and the aminolysis of **211** (equation 220) to yield acetoxime and ammonia appear not to be nitronate anion reactions.

O-Alkyl oximes (e.g. **214**) were observed on attempted acetylation of potassium 1-nitromethanenitronate (**213**) and 1-nitroethanenitronate with acetyl chloride or acetyl nitrate (52% yield of **214**)<sup>469</sup>

(equation 225). Some **214** (12 %) was also formed in the reaction of

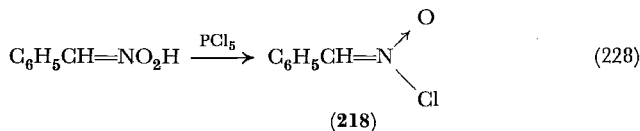


**213** with benzoyl chloride in which the benzoyl oxime **215** was produced<sup>469</sup> (equation 226). Formation of **214** suggests C-alkylation of an anhydride intermediate **216** by anion **217** (equation 227). Compound **214** has also been prepared from **217** and 1,1-dinitroethane<sup>478a</sup>.



### C. Nitronic Acid Halides

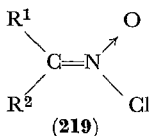
There are two published accounts purporting to describe nitronic acid chlorides<sup>32,479</sup>. In both instances the unstable oils obtained are very poorly characterized substances. Hantzsch and Veit<sup>32</sup> treated phenylmethanenitronic acid with phosphorous pentachloride. The product was said to be acid chloride **218** (equation 228),



an exceptionally unstable oil. A more vigorous reaction occurred with 4-nitrophenylmethanenitronic acid to yield 4-nitrophenyl-nitromethane<sup>32</sup>.

Reaction of nitroalkanes with picryl or *N*-(oxydichlorophosphino)pyridinium chloride at 80–120° produces low-boiling oils

(distilled from the reaction mixture and condensed in cold traps) and said to be nitronic acid chlorides **219**<sup>479</sup>. The compounds have the following colors; a, colorless; b and c, faint greenish blue; d,



- (a)  $\text{R}^1, \text{R}^2 = \text{H}, \text{H}$ ; b.p.  $2-3^\circ$ ; m.p.  $-43^\circ$   
 (b)  $\text{H}, \text{CH}_3$ ; b.p.  $5^\circ$   
 (c)  $\text{H}, \text{Et}$ ; b.p.  $5^\circ$   
 (d)  $\text{CH}_3, \text{CH}_3$ ; b.p.  $15^\circ$

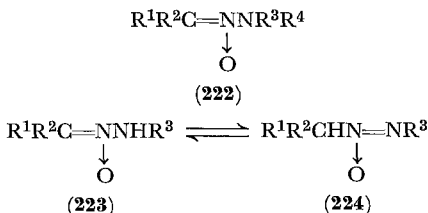
intense blue. With aqueous or ethanolic ferric chloride no colors are developed with the compounds. The blue colors suggest the presence of nitroso compounds **220**. 2-Chloro-2-nitropropane is known as a blue liquid b.p.  $70^\circ$  (760 mm)<sup>480</sup>. However, chloronitrosoalkanes



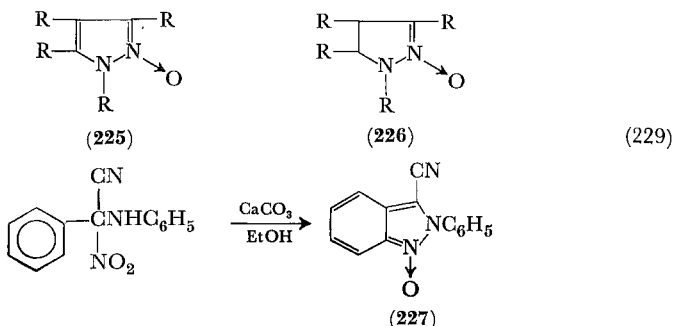
of the type  $\text{RCH}(\text{Cl})\text{NO}$  are known only in solution and readily isomerize to colorless  $\alpha$ -chlorohydroxamic acids **221**<sup>274a</sup>. It appears that the substances assigned structure **219** have not been adequately characterized, and an authentic nitronic acid chloride is yet to be described.

#### D. Nitronic Acid Amides

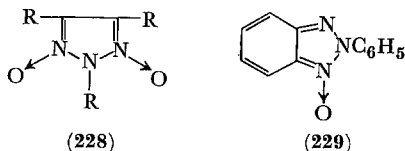
Nitronic acid amides are not well known. No substance having the hydrazone oxide structure **222** has been described. Nitronic acid amides of primary amides **223** would be azoxy tautomers **224**.



A cyclic nitronic acid amide ('lactam') would be a pyrazole oxide **225** or pyrazoline oxide **226**. Examples of the former are the indazole oxides; e.g. **227**<sup>481-484</sup> (equation 229).

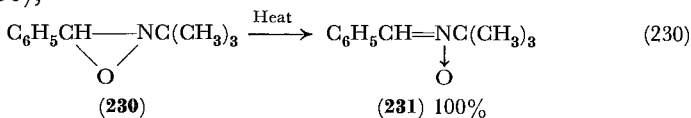


A nitronic acid imide would be a 2-*H*-1,2,3-triazole-1,3-dioxide (**228**); none has been described. However, 1-oxides such as **229** have been prepared<sup>485-487</sup>.



Nitronic acid amides could exist as reaction intermediates. Aminolysis of nitronic carboxylic anhydrides might involve a nitronic acid amide intermediate (equation 220).

Finally, nitrones (e.g. **231**) may be considered the 'ketones' of the nitronic acid series. They have not been prepared directly from nitronic acids, but are available from oxazirans (**230** → **231**)<sup>24,454,477</sup> (equation 230),



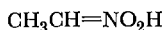
## VI. ANALYTICAL METHODS FOR NITRONIC ACIDS

Several methods are available for qualitative detection and quantitative determination of nitronic acids. Since tautomerization to the nitroalkane form often occurs readily in solution, the analytical method selected must consider this fact. The following tests do not apply to nitroalkanes. Some tests for nitronic acids are also applicable to nitronate anions.

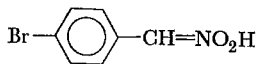
The ferric chloride test used for enolic substances may be applied to nitronic acids. A red color usually develops when aqueous or

alcoholic solutions of nitronic acids are treated with dilute ferric chloride solution<sup>1,13</sup>. Green<sup>85</sup> or brown<sup>33</sup> colors are also observed. This test, sometimes called the Konowalow reaction after its discoverer<sup>13</sup>, was employed by the early workers in nitronic acid

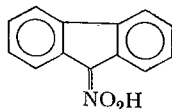
Colors with ferric chloride



Red



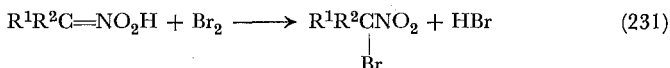
Deep brown



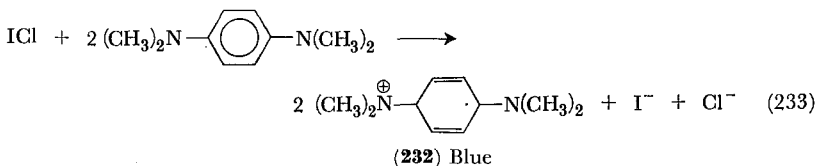
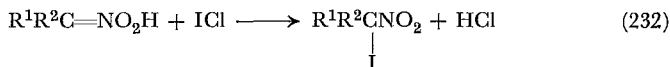
Dark green

chemistry<sup>1,13,159</sup>. The color is probably due to a  $\text{Fe}^{\text{III}}$  nitronate salt,  $\text{Fe}(\text{O}_2\text{N}=\text{CR}^1\text{R}^2)^{++}$ , similar to the colored  $\text{Fe}^{\text{III}}$  phenolate salts,  $\text{Fe}(\text{OAr})^{++488}$ . The test has been the basis for a quantitative colorimetric method<sup>489</sup>.

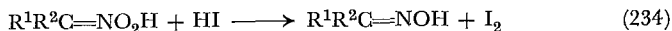
Bromine titration of nitronic acids occurs rapidly and is the basis of the Kurt Meyer analysis<sup>36</sup> (equation 231). Bromine or ferric chloride may be used as an indicator. Iodine monochloride has been



employed for quantitative analysis of nitronic acids<sup>209</sup> (equation 232). The unreacted iodine monochloride, which is employed in excess, is allowed to react with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine to produce the intensely blue Würster radical cation **232**, which may be assayed spectrophotometrically (equation 233).



The oxidizing property of nitronic acids is the basis of an excellent quantitative method<sup>276</sup>. A mixture of potassium nitronate salt and potassium iodide is acidified. The hydrogen iodide reacts with the liberated nitronic acid to produce iodine and an oxime (equation 234). The iodine is then titrated with sodium thiosulfate employing starch indicator.





Polarography has frequently been employed as a convenient method of quantitative analysis of nitronic acid-nitroalkane mixtures<sup>38,44,47,110,321,490</sup>. The nitronic acid form, as well as the nitronate anion, are not reduced polarographically at the dropping mercury electrode at the same voltage as nitroalkanes.

The greater acidity of nitronic acids ( $pK_a$  3–6) over the parent nitroalkanes ( $pK_a$  8–10) [ $\Delta pK_a = \text{ca. } 3\text{--}6$  (Figure 5)] is a property

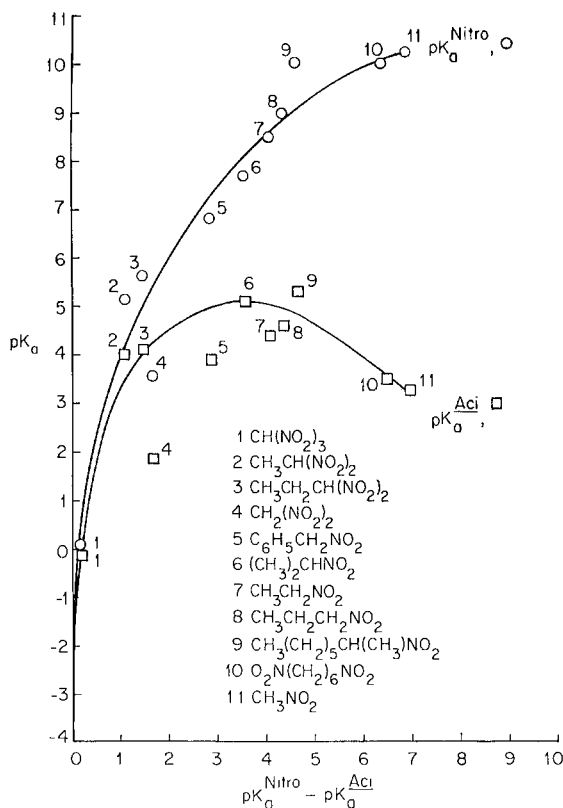


FIGURE 5. Plot of  $pK_a^{\text{Acid}}$  and  $pK_a^{\text{Nitro}}$  vs.  $pK_a^{\text{Nitro}} - pK_a^{\text{Acid}}$ . Data for nitronic acids and nitroalkanes in water at 25° in Table 5.

frequently employed for analysis. The nitronic acids are usually soluble in sodium bicarbonate solution<sup>1</sup>; most nitroalkanes are not (see  $pK_a$  values in Table 5, section II.D). Sodium hydroxide solution is not suitable for nitronic acid titration since nitroalkanes also react. 1,1-Dinitroalkanes and their nitronic acids are of nearly equal

acid strength ( $pK_a$  5–6); cf. Figure 5. Because of their relatively greater acidity, nitronic acids are better conductors in solution than nitroalkanes. The conductometric method has frequently been employed for quantitative analysis of those nitronic acids which have conductivities significantly greater than the corresponding nitroalkanes<sup>28–31,112</sup>.

A most convenient analytical method, useful for rapid determination—as in kinetic studies—takes advantage of the strong characteristic nitronic acid  $\pi - \pi^*$  ultraviolet absorption band in the ultraviolet region near  $240 m\mu$ <sup>52,53</sup>. Nitroalkanes do not absorb significantly in this region. Rapid reactions, such as *aci*-nitro tautomerization, may easily be followed by this spectrophotometric method<sup>52</sup>.

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## CHAPTER 8

# Activating effects of the nitro group in aromatic substitutions

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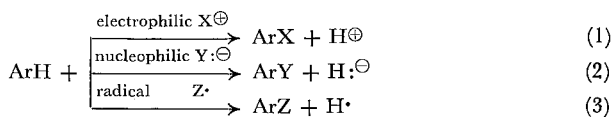
I. INTRODUCTION . . . . .	488
II. DISPLACEMENT OF HALOGEN IN NUCLEOPHILIC SUBSTITUTION REACTIONS OF AROMATIC NITROCOMPOUNDS . . . . .	492
1. The activating influence of the nitro group in halogen displacement	492
2. <i>Ortho</i> effects . . . . .	494
3. Displacement by amines . . . . .	499
4. Displacement by hydroxide . . . . .	507
5. Displacement by alkoxy- and phenoxyanions . . . . .	512
6. Halogen exchange . . . . .	512
7. Displacement by mercaptides . . . . .	515
8. Displacement by azide and thiocyanate anions . . . . .	515
9. Displacement by carbanions . . . . .	515
10. Displacement by sulfite, carboxylate, thiosulfones, etc. . . . .	516
11. Reactions of nitrohalobenzenes with miscellaneous reagents . . . . .	517
III. KINETICS AND MECHANISM . . . . .	518
1. Bond-making and bond-breaking as synchronous or non-synchronous processes . . . . .	518
2. Kinetics of two-step displacement . . . . .	520
3. Isotope effects . . . . .	530
4. The nature of intermediate complexes and transition states . . . . .	531
5. Effect of substituents in the substrate . . . . .	536
6. Steric effects . . . . .	540
7. Reactivity of halogens and comparison with other leaving groups . . . . .	542
8. Reactivity of nucleophiles . . . . .	549
9. Medium effects . . . . .	552



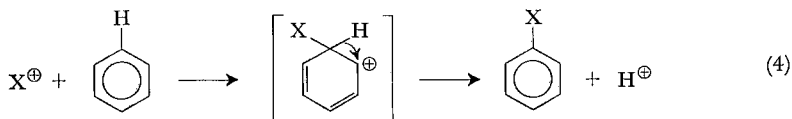
IV. NUCLEOPHILIC DISPLACEMENT OF OTHER GROUPS . . . . .	554
1. Displacement of hydrogen . . . . .	554
2. Displacement of nitro groups . . . . .	561
3. Displacement of alkoxy- and aryloxy groups in hydrolysis and trans- etherification . . . . .	565
4. Displacement of alkoxy- and aryloxy groups by amines . . . . .	569
5. Displacement of sulphonate ( $\text{OSO}_2\text{Ar}$ ) and other ester groups . . . . .	572
6. Displacement of amino and ammonium groups . . . . .	574
7. Displacement of miscellaneous groups . . . . .	575
V. DISPLACEMENTS IN POLYCYCLIC AND HETEROCYCLIC NITRO COMPOUNDS . . . . .	578
1. Displacements in polycyclic nitro compounds . . . . .	578
2. Displacements in heterocyclic nitro compounds . . . . .	581
VI. NUCLEOPHILIC PHOTOSUBSTITUTION . . . . .	582
1. Photochemical displacement of alkoxy groups . . . . .	582
2. Photochemical displacement of halogen . . . . .	585
3. Photochemical displacement of nitro groups . . . . .	586
VII. REARRANGEMENT REACTIONS . . . . .	587
1. The Smiles rearrangement . . . . .	587
2. The von Richter reaction . . . . .	591
3. Ring enlargement of polynitroaromatics . . . . .	595
VIII. REFERENCES . . . . .	598

## I. INTRODUCTION

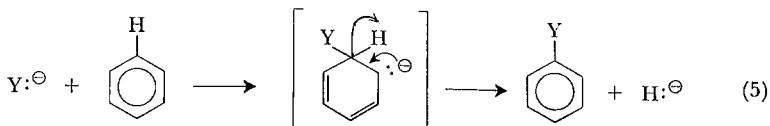
The three well known types of electrophilic, nucleophilic and radical aromatic substitution reflect a classification based on the nature of the attacking species (equations 1–3),



In electrophilic substitution (equation 1) an electron-deficient species  $\text{X}^\oplus$ , actually or potentially present in the reagent, displaces hydrogen as a *proton*. Two  $\pi$ -electrons from the aromatic substrate are localized for C—X bond-making, and the temporarily disrupted aromatic  $\pi$ -electron sextet is restored by heterolytic C—H bond-breaking (equation 4),

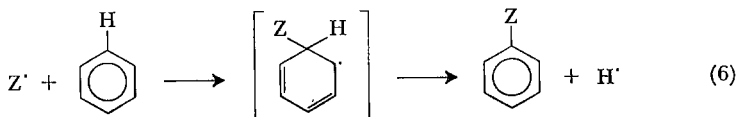


In nucleophilic substitution (equation 2) an electron-donating species  $Y^{\ominus}$  supplies the electrons for a new C—Y bond. Again the aromatic sextet is temporarily sacrificed and subsequently restored by elimination of a *hydride ion* from the anionic intermediate (equation 5).



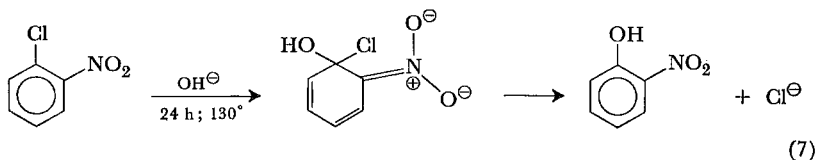
In these heterolytic processes the *two* electrons for the new  $\sigma$ -bond are supplied either by the substrate or by the reagent.

In radical substitutions the process is homolytic (equation 3); substrate and reagent each contribute one electron to the new bond and formally a *hydrogen atom* is displaced (equation 6).



Despite a formal similarity between the heterolytic processes (equations 1 and 2) nucleophilic displacement of hydrogen is rarely observed and occurs only when the intermediary anion is stabilized by electron-withdrawing substituents at suitable positions in the substrate. The strongly electron-attracting nitro group is eminently suited to favor such stabilization. For instance nitrobenzene gives considerable quantities of *o*-nitrophenol when heated with powdered, super-dry potassium hydroxide, whereas unsubstituted benzene under similar conditions does not yield a trace of phenol.

Direct introduction of a hydroxyl group in an aromatic nucleus is effected under less drastic conditions by nucleophilic displacement of halogen (or other groups with greater anionic stability than hydrogen) especially when nitro groups are present in *ortho*- and *para*-positions (equation 7),



This *activating* effect of nitro groups in nucleophilic displacements is

TABLE I. Reviews on various aspects of nucleophilic aromatic substitution.

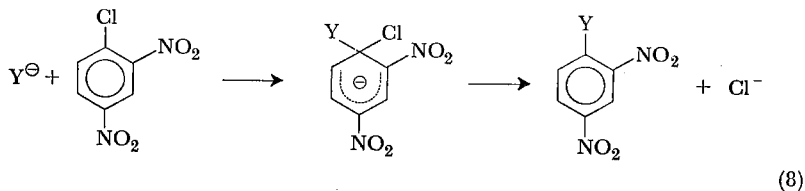
Reviews by:	Number of ref.	Date	Ref.
J. F. Bunnett and R. Zahler	621	1951	1
J. Miller	37	1951	2
C. K. Ingold	57	1953	3
G. S. Hammond and M. F. Hawthorne	25	1956	4
J. F. Bunnett	38	1958	5
J. F. Bunnett	91	1958	6
J. Sauer and R. Huisgen	174	1960	7
B. Capon and C. W. Rees	12	1962	8
R. F. Hudson	89	1962	9
J. F. Bunnett	141	1963	10
B. Capon and C. W. Rees	19	1963	11
S. D. Ross	102	1963	12
B. Capon and C. W. Rees	40	1964	13
G. Illuminati	144	1964	14
H. Zollinger	22	1964	15
R. G. Sheperd and J. L. Fredrick	813	1965	16
R. Foster and C. A. Fyfe	130	1966	17

in sharp contrast with the deactivating influence on electrophilic displacement of hydrogen. Variation of nucleophilic agent, leaving groups and activating substituents in the nitroaromatic substrate leads to a profusion of combinations.

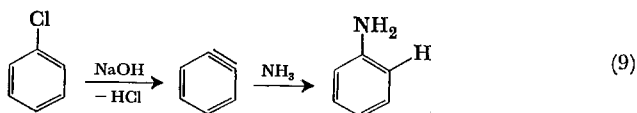
By far the most important class of reactions is formed by the halogen displacements and these are therefore separately discussed in section II. Much attention has been paid to the mechanism of halogen displacement (section III).

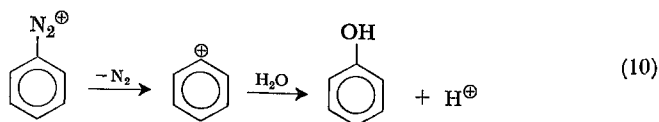
In many reviews on nucleophilic aromatic substitution usually three mechanisms are considered (equations 8–10).

(a) *Addition-elimination mechanism:*



(b) *Elimination-addition mechanism:*



(c)  $S_N1$ -mechanism:

It will turn out that in nitroaromatic systems the addition-elimination mechanism operates almost exclusively. This involves a more or less stable intermediate complex, as already advocated in the earliest and most extensive review by Bunnett and Zahler<sup>1</sup> and by Miller<sup>2</sup>. In a way these have sparked research on many theoretical and practical aspects of nucleophilic aromatic substitution, so much so that several reviews have appeared to record the rapid progress (Table 1). In Table 2 the authors are assembled who have been most active in the field.

TABLE 2. Significant publications in the field of nucleophilic substitution in aromatic nitro compounds.

Series of papers by:	Field of interest	Ref.
C. W. L. Bevan and coworkers	Mechanism, kinetics	18-31
H. Zollinger	Mechanism, kinetics	15, 32,
C. F. Bernasconi and coworkers	Mechanism, kinetics	33-40
J. A. Brioux and coworkers	Mechanism, kinetics	41-51, 379-381
J. F. Bunnett and coworkers	Mechanism, kinetics	1, 5, 6, 10, 52-78
N. B. Chapman and coworkers	Mechanism, kinetics, heterocyclic	79-90
F. Pietra and coworkers	Mechanism, kinetics	91-96
A. J. Parker and coworkers	Mechanism, kinetics	97-101
S. D. Ross and coworkers	Mechanism, kinetics	12, 102-111
H. Suhr	Mechanism, kinetics	112-118
J. Miller and coworkers	Mechanism, kinetics, theory	2, 287 119-161
J. Murto and coworkers	Mechanism, kinetics, theory	162-181
M. Simonetta	Theory, mechanism, kinetics	182-193
V. Gold and coworkers	Complexes, mechanism, kinetics	194-210
R. Foster and coworkers	Complexes	17, 211-228
S. S. Gitis and coworkers	General, Yanovski reaction, transesterification	229-256
L. M. Litvinenko and coworkers	General	257-264
E. Havinga and coworkers	Photochemistry	265-276

Unlike most reviews the present chapter deals exclusively with aromatic nitro compounds with an emphasis on principles, mechanisms, and recent advances in practice and theory of the topic dating from the last fifteen years (up till mid-1967).

## II. DISPLACEMENT OF HALOGEN IN NUCLEOPHILIC SUBSTITUTION REACTIONS OF AROMATIC NITRO COMPOUNDS

### I. The activating influence of the nitro group in halogen displacement

When an electron attracting nitro group is linked to an aromatic system it gives rise to centers of low electron density located at certain ring carbon atoms, which are therefore preferentially attacked by nucleophilic reagents. In activating power the nitro group is only surpassed by such strongly electronegative groups as  $\text{CF}_3\text{SO}_2$ ,  $\text{N}_2^+$  and  $\text{NO}$ . There is no general agreement about the relative activating power of these and other groups<sup>26, 125, 139, 140, 142, 146, 147, 242, 277</sup> mostly because of substrate dependence.

The nitro group is an *ortho-para* activating substituent, the *ortho*-effect being stronger<sup>278, 279</sup> than the *para*-effect. This order can be reversed, e.g. by steric factors. In the review of Bunnett and Zahler<sup>1</sup> the activating power of the nitro group at various positions in the ring is discussed extensively. In Table 3 some typical examples are collected.

Displacements of halogens from nitroaromatic molecules are in general smooth reactions with good yields (>80 %).

From a comparison of activation parameters it follows that the nitro group affects mainly the activation energy, while there is no direct influence on the activation entropy. Activation energies for the methoxydechlorination (replacement of chlorine by methoxyl) of chloronitrobenzenes were calculated by Miller<sup>153</sup> (cf. Table 4 and section III.4).

In studies of the activating effects of the *ortho*-nitro group for reactions with amines the effect of so called *built-in solvation* (cf. section II.2) has to be taken into account. This lowers the activation energy as is illustrated by comparison of the last two examples in Table 3, and furthermore in Table 5, where it can be seen that introduction of an *ortho*-nitro group is 10 to 100 times more effective for reaction with piperidine than for reaction with methoxide. This is also found in the nitronaphthalene series<sup>186, 187, 282</sup>. In the naphthalene series

TABLE 3. *Relative activating power of o-, m- and p-nitro groups in aromatic nucleophilic substitution. Rate ratios,  $k_{\text{para}} \equiv 1$  (cf. reference 1).*

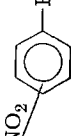
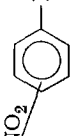
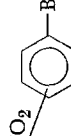
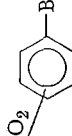
Type of reaction	Temp. °C	Position of the NO <sub>2</sub> -group(s)						Ref.
		Unsubstituted	<i>m</i> -NO <sub>2</sub>	<i>o</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>	3,5-(NO <sub>2</sub> ) <sub>2</sub>	2,4-(NO <sub>2</sub> ) <sub>2</sub>	
 -F + MeO <sup>-</sup> /MeOH, MeO <sup>-</sup> /MeOH	49.55	1.34 × 10 <sup>-9</sup>	6.70 × 10 <sup>-3</sup>	0.675	1.00	1.77	2.39 × 10 <sup>3</sup>	22
 -I + <sup>131</sup> I <sup>-</sup> in acetonitrile	50	0.75 × 10 <sup>-9</sup>	5.43 × 10 <sup>-5</sup>		1.00		1.17 × 10 <sup>6</sup>	120, 144
	0				1.00			156
	157	2.37 × 10 <sup>-5</sup>	2.54 × 10 <sup>-3</sup>	9.35	1.00			280
	238	5.24 × 10 <sup>-4</sup>	1.69 × 10 <sup>-3</sup>	3.35	1.00			
+ MeS <sup>-</sup> in MeOH	0				1.00		1.17 × 10 <sup>4</sup>	156
 -Br + piperidine in benzene, reflux		very slow	2.53 × 10 <sup>-3</sup>	205	1.00			281
 -Br + EtO <sup>-</sup> /EtOH	20	~10 <sup>-8</sup>		~0.2	1.00		3 × 10 <sup>4</sup>	190

TABLE 4. Energies of activation for the methoxydechlorination of chloronitrobenzenes<sup>153</sup>.

Substrate	$\Delta E$ kcal/mole	
	calculated	Observed value
2,4,6-trinitrochlorobenzene	13.5	
2,4-dinitrochlorobenzene	19.0	17.4
<i>p</i> -nitrochlorobenzene	24.0	24.1
chlorobenzene	50-55	

TABLE 5. Relative rates for reactions of 2,4-dinitro- and 4-nitrohalobenzenes with ethoxide and piperidine.

Reagent	$\frac{k_{2,4-(NO_2)_2}}{k_{4-NO_2}}$		Ref.
	Chlorobenzene	Bromobenzene	
MeO <sup>-</sup> in MeOH or EtO <sup>-</sup> in EtOH at 60°	$2.6 \times 10^4$	$0.80 \times 10^4$	18, 186 41, 119
piperidine in benzene at 25°	$0.96 \times 10^6$	$0.45 \times 10^6$	121, 283

introduction of a nitro group in the 'second' ring, e.g. the 5-position, has a relatively small activating effect<sup>182, 188, 189</sup>.

In the abundance of work where the nitro group only functions as an activating substituent it must not be forgotten that the nitro group itself is also easily displaced when present in appropriately substituted aromatics (cf. IV.2).

## 2. Orthoeffects

It has been known for a long time that there is a considerable difference in the reactivity of *o*-nitro- and *p*-nitrohalobenzenes towards various nucleophiles. This is partly shown in Tables 3 and 5, and more systematically in Table 6. It is remarkable that for reactions with anionic reagents the *para* isomer is nearly always more reactive than the *ortho* isomer, whereas for reactions with primary or secondary amines it is just the other way round. The exceptions to this rule pertain to a few reactions of anions with *o/p*-nitrofluorobenzenes. In the activation of *ortho*- and *para*-positions the  $-M$  effect of the nitro group generally plays an important role<sup>278</sup>. To exert its mesomeric effect fully the nitro group must be coplanar with the aromatic

TABLE 6. Relative reaction rates of *o*- and *p*-nitrohalobenzenes and a few sulphonates with various nucleophiles.

X	Reagent	Solvent	Temp. °C	$\frac{k_{ortho}}{k_{para}}$	Ref.
F	MeO <sup>-</sup>	MeOH	0	1.05	128, 132
			50	0.685	
			100	0.500	
	EtO <sup>-</sup>	dioxan	25	0.54	286
		MeOH	49.5	0.675	22
		EtOH	61	1.34	18, 20
Cl	MeO <sup>-</sup>	MeOH	25	1.13	286
			85	0.268	1
			50	0.354	123
			81.6	0.290	119, 287
			100.8	0.274	119, 287
			50	0.297	125, 126
	EtO <sup>-</sup>	dioxan	0	0.334	128, 132
			50	0.298	128, 132
			100	0.274	128, 132
			25	0.300	286
			25	0.407	286
			25.3	0.156	58, 61
Br	PhS <sup>-</sup>	60% dioxan-H <sub>2</sub> O	25.3	0.156	58, 61
		DMF	100	0.82	288
	-CH(COOEt) <sub>2</sub>	MeOH	0	0.191	128, 132
			50	0.247	
			100	0.299	
			100	0.374	
I	MeO <sup>-</sup>	MeOH	0	0.175	128, 132
			50	0.272	
			100	0.374	
F	piperidine	EtOH	70	4.37	85
			80	4.95	
			90	5.11	
	morpholine	EtOH	70	5.53	85
			80	6.00	
			90	6.08	
Cl	piperidine	benzene	60	55.1	46
			75	59.3	
			100	61.6	
		MeOH	60	2.19	46
			75	2.11	
			100	2.46	
	piperidine	EtOH	60	2.23	46
			75	2.35	
			100	2.63	
		1% dioxan	102	1.35	58
		75% MeOH-H <sub>2</sub> O	102	1.75	58
		93% EtOH-H <sub>2</sub> O	102	2.34	58, 59



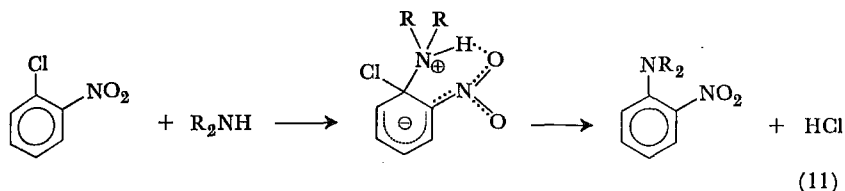
TABLE 6. (*continued*)

X	Reagent	Solvent	Temp. C°	$\frac{k_{ortho}}{k_{para}}$	Ref.
Br	1,4-diazabicyclo- [2,2,2]octane piperidine	99.8% EtOH	102	2.98	58, 85
		benzene	102	46.8	41, 58
		xylene	116	80	58, 284
		EtOH	70	2.60	85
			80	2.65	
			90	2.76	
		benzene	75	49.8	41, 43, 44
			100	46.3	
		benzene	100	166	47
		EtOH	100	2.5	47
		benzyl alcohol	120	5.6	110
		benzyl alcohol	150	0.004	110
	morpholine	EtOH	70	3.57	85
			80	3.80	
			90	4.02	
			45	39.2	41
			75	41.5	
	-OSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub> { piperidine	60% dioxan-H <sub>2</sub> O	70	3.78	85
			80	3.98	
			90	4.00	
	-OSO <sub>2</sub> C <sub>6</sub> H <sub>2</sub> -2,4,6-(CH <sub>3</sub> ) <sub>3</sub> { piperidine	60% dioxan-H <sub>2</sub> O	46	2.66	75
			46	2.30	75

nucleus. This is easily realized in *p*-nitrohalobenzenes but less readily in the isomeric *o*-nitro compounds, particularly when the halogen atom is bulky. This explains why most *ortho*-nitro compounds are less reactive than their *para*-isomers, and it explains also the 'exceptional' behavior of *o*-nitrofluorobenzene where the steric effect is smallest<sup>18,20,22</sup>. The field effect of the fractional negative charge on the nitro group might also hinder the approach of a negatively charged nucleophilic species<sup>60,284,285</sup> but the importance of this latter effect has been questioned<sup>60</sup>.

The disturbing question remains why anionic nucleophiles should respond to the *ortho*effect so markedly different from primary and secondary amines. This can be understood by accounting for a strong charge separation in the intermediate state when a nitrohalobenzene reacts with an amine (for arguments supporting the nature of the intermediate state, see III, 1-4). In the *ortho*-isomers

the importance of *intramolecular* hydrogen-bonding between the N—H and the *ortho*-nitro group<sup>30,79,81,285</sup> in the intermediate complex has been stressed (cf. also section III, 1-4) (equation 11).



In accordance with this theory, Ross and coworkers<sup>110,111</sup> have found that tertiary amines with no possibility for intramolecular hydrogen bonding react with *o/p*-nitrohalobenzenes (cf. Table 6) analogous to anionic nucleophiles, i.e. with an *o/p* rate ratio larger than unity. Furthermore, kinetic studies have produced evidence in favor of hydrogen bonding effects<sup>50</sup> (cf. also reference 284).

Bunnett and coworkers<sup>5,60</sup> introduced the concept of 'built-in solvation', being the electrostatic interaction between the positive charge on the *N*-atom and the negative charge on the nitro group thus accounting for the specific *ortho* effects. At our present state of knowledge it seems more appropriate to define built-in solvation as all of the intramolecular interactions which lead to a stabilization of the intermediate complex. It is not clear which effect predominates, the intramolecular hydrogen bonding or the built-in solvation according to Bunnett.

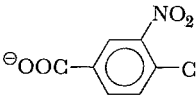
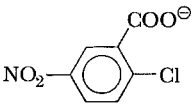
Because of these built-in solvation effects the intermediate complex (cf. section III.4) is more stabilized for the *ortho*-isomer than for the *para*-isomer, which explains the higher reaction rate for the former, resulting in a high *ortho/para* ratio (cf. Table 6). Because of the large charge separation in the intermediate complex reaction rates should depend very much on the solvent polarity. The reactivity of the *para*-isomer is considerably lowered in nonpolar solvents and this explains the large *ortho/para* ratio in these solvents (cf. Table 6). It can also be seen from Table 6 that the *ortho/para* ratio increases at higher temperatures, presumably because intermolecular solvation is then less effective. The substitution of the *ortho*-isomer is much less sensitive for (external) solvent effects because of the built-in solvation.

In most studies no attention is paid to catalytic effects on the *ortho/para* rate ratio. When the second step of the reaction, i.e. expulsion of halide ion, appears in the rate equation, this probably

occurs to a different extent for the *ortho* and *para* isomers, as indicated by a study of Sbarbati and coworkers<sup>47</sup> (cf. section III.2).

This type of *ortho* effect is not confined to the nitro group only. A similar effect is found for the carboxylate group<sup>123,125,126</sup>, where the concept of built-in solvation for reaction with amines can also be used<sup>59</sup>, be it hydrogen bonding or electrostatic interaction. The carboxylate group is activating in all cases except when situated at the *ortho* position with respect to halogen in the reaction with methoxide ion (cf. Table 7). Here the difficult approach of the anion

TABLE 7. The effect of built-in solvation for the carboxylate group as shown by comparison of the rate of chlorine displacement from nitrochlorobenzoic acids and nitrochlorobenzene.

Reaction	$k_{\text{COO}^-}/k_{\text{H}}$
	<p>piperidine 3.48</p> <p>MeO<sup>-</sup> 7.5</p>
	<p>piperidine 33.0</p> <p>MeO<sup>-</sup> 0.35</p>

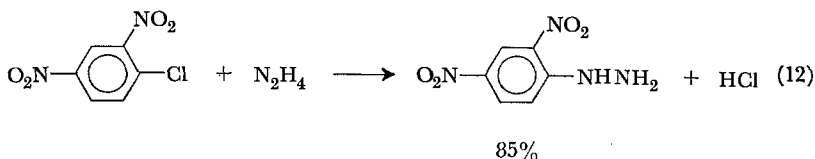
towards the negatively charged —COO<sup>-</sup> is probably the main cause of deactivation.

The *ortho* effect is also important in reactions of the 2,4-dihalo-nitrobenzenes where the *ortho*-halogen is replaced much more rapidly than the *para*-halogen (cf. reference 58 and references therein). The selectivity was demonstrated by Greizerstein and Brieux<sup>46</sup> who found that in reaction of piperidine with 2,4-dichloronitrobenzene-4-<sup>36</sup>Cl *ortho*-displacement occurred nearly exclusively in benzene while in methanol as the solvent the *ortho-para*-displacement ratio was 12.5:1 (cf. also reference 289).

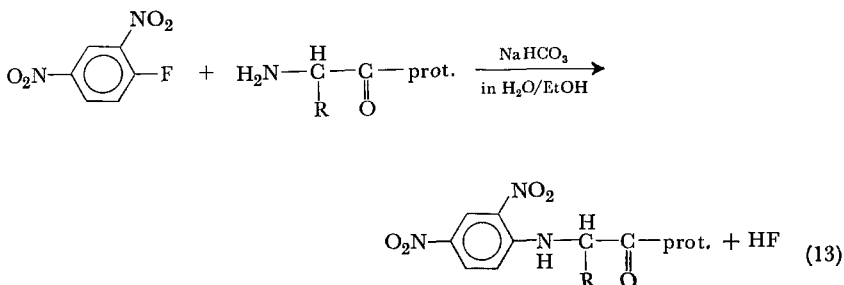
Brieux and coworkers<sup>49</sup> compared the kinetics of the reactions of 4-, 5- and 6-substituted 1-chloro-2-nitrobenzenes with sodium thiophenoxide in methanol. The polar influence of a substituent in *ortho*-position to chlorine predominates over its steric effect.

### 3. Displacement by amines

By far the most extensively applied nucleophiles in halogen displacement are the amines. Substitution products are easily obtained in yields of 80–90% simply by reaction in a suitable solvent (often benzene or alcohol) at temperatures between 0–100°. Reaction is usually complete within a few hours, and with strongly activated compounds such as picric chloride even within a few minutes. For instance the well known carbonyl reagent 2,4-dinitrophenylhydrazine is prepared by refluxing the corresponding chloride with an aqueous alcoholic solution of hydrazine for one hour<sup>290</sup> (equation 12).



Sanger's standard determination of *N*-terminal amino acids in proteins with 2,4-dinitrofluorobenzene is another practical application of nucleophilic substitution<sup>291</sup> (equation 13).



Hydrolysis gives an *N*-(2,4-dinitrophenyl)amino acid, easily characterized by paper- or thin-layer chromatography.

Most other examples in Table 8 involve rate studies, covering the last 15 years. Further substitutions by amines are given in Table 28, where the accent is on comparative displacement rates of the various halogens and their theoretical interpretations (cf. section III.8, and references 113, 116–118).

TABLE 8. Nucleophilic displacement of halogen from nitrohalobenzenes.



X	Position NO <sub>2</sub>	Other substituents in nitroaromatic	Amine (prim., sec. or tert.)	Solvent	Ref.
F	2	3,4,5,6-F <sub>4</sub>	piperidine	EtOH	85
			morpholine	EtOH	85
			NH <sub>3</sub> , MeNH, Me <sub>2</sub> NH	MeOH	285
F	4		Me <sub>2</sub> NH	DMF	151
			NH <sub>3</sub>	MeOH	73
			RNH <sub>2</sub>	DMSO	113, 116
			R <sub>1</sub> R <sub>2</sub> NH	DMSO	113, 117
			piperidine	benzene	91
				DMSO	95, 114
				EtOH	85
				MeOH	73, 118
			several	112	
			DMSO	95	
			DMSO	95	
			EtOH	85	
			MeOH	23	
			MeOH	73	
			2-methylpiperidine		
			2,6-dimethylpiperidine		
			morpholine		
			aniline		
			NH <sub>3</sub> , piperidine		
		2-Me			

F	2,4	2-Br	NH <sub>3</sub> , piperidine	MeOH	73
			Et <sub>3</sub> NH, <i>i</i> -Pr <sub>3</sub> NH, morpholine, NH <sub>3</sub> , piperidine	MeOH, <i>t</i> -BuOH	118
			MeNH <sub>2</sub> , EtNH <sub>2</sub> , Me <sub>3</sub> NH, NH <sub>3</sub>	H <sub>2</sub> O	118
			NH <sub>3</sub>	MeOH	292
			<i>n</i> -BuNH <sub>2</sub>	MeOH	293
			NH <sub>3</sub> liq.		216
			benzylamine	benzene	37
			piperidine (catalyzed)		91, 33, 34, 35,
			<i>n</i> -d-piperidine	benzene	39, 96
			piperidine	MeOH	67, 73
			2-methylpiperidine	benzene	93
			2,6-dimethylpiperidine	benzene	93, 94
			piperidine (catalyzed)	benzene	76, 91, 96
			morpholine	benzene	40
			<i>N</i> -d <sub>2</sub> -anisidine		32, 33
			anilines	EtOH	79, 80, 294, 295
			<i>N</i> -methylaniline	nitrobenzene	294
			<i>N</i> -methylaniline	EtOH	72, 294
			aniline	acetone	30
			pyridine	acetone	30
			<i>N</i> -methylaniline	60% dioxan	72
			aniline	MeOH, <i>t</i> -BuOH	293
			aniline	60% dioxan-H <sub>2</sub> O	293
F	2,6		<i>p</i> -anisidine	benzene	36
			NH-heteroaromatic compds.	various	296
F	2,4,6		aniline	EtOH	279
			NH <sub>3</sub> liq.		216
			aniline	EtOH	295
			NEt <sub>3</sub>	chloroform	102

(continued)

TABLE 8. (*continued*)

X	Position NO <sub>2</sub>	Other substituents in nitroaromatic	Amine (prim., sec. or tert.)	Solvent	Ref.
Cl	2	piperidine		benzene	41, 46, 47, 50
				EtOH	46, 47, 80, 85
				MeOH	46
				EtOH-H <sub>2</sub> O	58
				MeOH-H <sub>2</sub> O	58
		piperidine		dioxan-H <sub>2</sub> O	58
				benzene	43, 44, 45, 51
				benzene	43, 44, 45, 49, 89
				EtOH-H <sub>2</sub> O	59
				benzene	43, 44
		4-R 5-R 4-R 6-R 3-R 5- <sup>36</sup> Cl 4-CF <sub>3</sub>		benzene	43, 44
				benzene, MeOH	46
				benzene	51
				xylene	284
				xylene	284
Cl	4	5-R 6-R		PhCH <sub>2</sub> OH	110
				PhCH <sub>2</sub> OH	110
				MeOH	49, 297
				benzene	48
				dioxan-H <sub>2</sub> O	298
		piperidine NHMe <sub>2</sub> piperidine		EtOH	46, 47, 80, 85
				benzene	41, 43, 44, 46, 47, 50
				EtOH-H <sub>2</sub> O	58, 59
				DMSO	113, 114
				MeOH-H <sub>2</sub> O	58
		1,4-diazabicyclo[2.2.2]octane			
		piperidine n-d-piperidine piperidine			

	piperidine	dioxan-H <sub>2</sub> O	58
	<i>N</i> - <i>d</i> -piperidine	xylenes	284
	piperidine	MeOH	284
		PhCH <sub>2</sub> OH	46
			110
	Et <sub>2</sub> NH, PhCH <sub>2</sub> NH <sub>2</sub> , (HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH, heterocyclic amines	DMSO	113
	1,4-diazabicyclo[2.2.2]octane	PhCH <sub>2</sub> OH	110
2-R	piperidine	EtOH-H <sub>2</sub> O	59
2-R	piperidine	benzene	43, 44
3-R	piperidine	benzene	43, 44
	NH <sub>3</sub>	MeOH	292
	NH <sub>3</sub>	DMSO	169
	NH <sub>3</sub>	EtOH	283, 299
	prim. aliphatic amines	EtOH	283
	sec. aliphatic amines	EtOH	104, 283
	( <i>t</i> -Bu) <sub>3</sub> N, <i>t</i> -BuNH <sub>2</sub> , <i>n</i> -BuNH <sub>2</sub>	EtOH	103, 104, 107, 300, 301
	allylamine	CHCl <sub>3</sub>	108
	<i>n</i> -BuNH <sub>2</sub>	CHCl <sub>3</sub>	104, 105, 107, 108
		aq. dioxan	106, 107
	<i>t</i> -BuNH <sub>2</sub>	DMF; EtOH	107, 302
	( <i>n</i> -Bu) <sub>2</sub> NH	CHCl <sub>3</sub>	104
	PhCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	CHCl <sub>3</sub>	104
	PhCH <sub>2</sub> NH <sub>2</sub>	MeOH-DMSO	303
	allylamine	CHCl <sub>3</sub> /EtOH	109
	1,4-diazabicyclo[2.2.2]cyclooctane	MeCN	111
	piperidine	DMSO	303
	piperidine	MeOH	60, 67, 68, 190, 304
		aq. MeOH	60, 304
		aq. dioxan	55, 60, 68, 78

(continued)





			piperidine; aniline		
		6-R	NH <sub>3</sub> liq	EtOH	86
		6-R	NH <sub>3</sub> liq		216
		3-Cl	aniline		216
	2,6		NH <sub>3</sub>		190, 279
Cl	2,4,6		aniline		216, 299
Cl			subst. anilines		190, 295
			anilines	benzene	257-264
		3,5-Cl <sub>2</sub>	NH <sub>3</sub> liq	MeOH	23
			piperidine		216
Br	2		piperidine	piperidine	308
			piperidine	benzene	41, 281
			piperidine	EtOH	80, 85
			morpholine	EtOH	85
		4-R	piperidine	piperidine	309
		various			
		Me-subst.	piperidine	benzene	281
			piperidine	benzene	281
		3,5-Cl <sub>2</sub>	NH <sub>3</sub> liq		216
Br	3	5,6-Cl <sub>2</sub>	H <sub>2</sub> NNH <sub>2</sub>		310
		various			
		Me-subst.	piperidine	benzene	281
			piperidine	DMSO	114
			piperidine	benzene	41, 53, 311
			piperidine	EtOH	80, 85
			morpholine	EtOH	85
			NH <sub>3</sub> liq		216
			NH <sub>3</sub>	MeOH	292
			<i>t</i> -BuNH <sub>2</sub>	DMF	107
			<i>n</i> -BuNH <sub>2</sub>	CHCl <sub>3</sub>	107
Br	2,4		piperidine	MeOH	67, 190
			aniline	EtOH	79, 190, 294, 295

(continued)

TABLE 8. (continued)

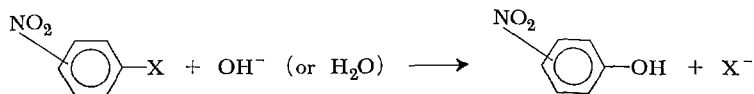
X	Position NO <sub>2</sub>	Other substituents in nitroaromatic	Amine (prim., sec. or tert.)	Solvent	Ref.
			substituted anilines		
			n-methylaniline	EtOH	79
			n-methylaniline	PhNO <sub>2</sub>	294
			H <sub>2</sub> NNH <sub>2</sub>	EtOH	72, 294
Br	2,6	4,5-Br <sub>2</sub>	aniline		310
Br	2,4,6		NH <sub>3</sub>	EtOH	190, 279
			aniline		216
			NH <sub>3</sub>	EtOH	295
I	2		piperidine	benzene	216
			piperidine	EtOH	41
I	4		piperidine	benzene	85
			piperidine	EtOH	41
			piperidine	EtOH	85
			pyrrolidine, morpholine, pyrrole, Et <sub>2</sub> NH, PhCH <sub>2</sub> NH <sub>2</sub> , (HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH	DMSO	113, 114
I	2,4		NH <sub>3</sub> liq	DMSO	113
			n-BuNH <sub>2</sub>		216
			i-BuNH <sub>2</sub>	CHCl <sub>3</sub> ; DMF	107
			NH <sub>3</sub>	DMF	107
			piperidine	MeOH	292
			piperidine	MeOH	67
			aniline	aq. dioxan	68
			subst. anilines	EtOH	79, 295
I	2,6		aniline	EtOH	79
I	2,4,6		aniline	EtOH	279
			aniline	EtOH	295

R = alkyl.

#### 4. Displacement by hydroxide

Although hydroxides are generally somewhat less reactive than amines in halogen displacement (cf. section III.8), they react under relatively mild conditions especially with halobenzenes containing two or three nitro groups in *o/p*-positions (Table 9).

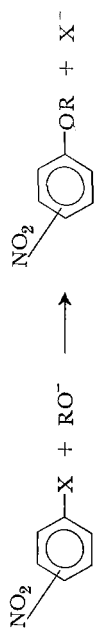
TABLE 9. Nucleophilic displacement of halogen from nitrohalobenzenes by  $\text{OH}^-$  or water.



X	Position NO <sub>2</sub>	Other substituents	Reagent	Solvent	Ref.
F	4	—	$\text{OH}^-$	50% dioxan	73
		—	$\text{NaOH-H}_2\text{O}$	DMSO	168
		2-Me	$\text{OH}^-$	50% dioxan	73
		2-Br	$\text{OH}^-$	50% dioxan	73
F	2,4	—	$\text{OH}^-$	$\text{H}_2\text{O}$	173, 176
		—	$\text{OH}^-$	50% dioxan	73
		—	$\text{NaOH-H}_2\text{O}$	DMSO	168
		—	$\text{H}_2\text{O}$	DMSO	168
		—	$\text{NaOH/ROH}$	$\text{ROH-H}_2\text{O}$	166, 167
		—	$\text{NaOH/ROH}$	$\text{ROH-H}_2\text{O}$	167
		—	$\text{H}_2\text{O}$	$\text{H}_2\text{O}$	174, 175
F	2,4,6	—	$\text{NaOH-ROH}$	$\text{H}_2\text{O-ROH}$	174
		—	$\text{NaOH}$	$\text{H}_2\text{O}$	174, 175
		—	$\text{H}_2\text{O-ROH}$		174
		—	$\text{KOH}$	$\text{EtOH-H}_2\text{O}$	184
Cl	2	—	$\text{OH}^-$	60% dioxan- $\text{H}_2\text{O}$	55
Cl	4	4-Br	$\text{OH}^-$	dioxan- $\text{H}_2\text{O}$	298
Cl	2,4	—	$\text{OH}^-/\text{RO}^-$	$\text{ROH-H}_2\text{O}$	304
		—	$\text{OH}^-$	$\text{H}_2\text{O}$	162, 173
		—	$\text{OH}^-$	$\text{ROH and H}_2\text{O-ROH}$	162
		—	$\text{OH}^-$	60% dioxan- $\text{H}_2\text{O}$	55
		—	$\text{NaOH}$	10% dioxan- $\text{H}_2\text{O}$	78
Cl	2,6	4- $\text{CO}_2^-$	$\text{OH}^-$	$\text{H}_2\text{O}$	129
			$\text{H}_2\text{O}$	$\text{H}_2\text{O}$	299
Cl	2,4,6	—	$\text{NaOH}$	$\text{H}_2\text{O}$ (trace $\text{EtOH}$ )	312
		—	$\text{OH}^-$	acetone	313
		—	$\text{NaOH}$	$\text{H}_2\text{O}$	175, 314
		—	$\text{H}_2\text{O}$	$\text{H}_2\text{O}$	175, 299
		—	$\text{NH}_4\text{OH}$	acetone	315, 316
		—	$\text{NaOH}$	acetone	316
Br	2,4	—	$\text{OH}^-$	$\text{H}_2\text{O}$ and $\text{ROH}$	162

R = alkyl

TABLE 10. Nucleophilic displacement of halogen from nitrohalobenzenes by alkoxides and certain phenoxides.

Position		Substituent		Reagent		Solvent		Ref.	
X	NO <sub>2</sub>								
F	4	MeO <sup>-</sup>				several		303	
						MeOH		22, 23, 70, 73, 120, 128, 132, 139, 140, 144, 152, 160	
						MeOH, MeOH-H <sub>2</sub> O		304	
						MeOH-DMSO		303	
		EtO <sup>-</sup>				EtOH, EtOH-H <sub>2</sub> O		304	
						EtOH		18	
						dioxan		286	
						MeOH-DMSO		303	
						dioxan		286	
						MeOH		23	
F	2					MeOH, EtOH, <i>i</i> -PrOH		150	
		2-Me				MeOH		73	
		2-Br				MeOH		73	
						dioxan		286	
						MeOH		22, 132, 139	
						MeOH/ether		285, 318	
		3,4,5,6-F <sub>4</sub>				MeOH-H <sub>2</sub> O		24	
						dioxan		286	
						EtOH		20	

F	3	4-R (R-F, Cl, Br, I, NH <sub>2</sub> , NO <sub>2</sub> )	EtO <sup>-</sup>	EtOH	20
		4 <sup>⊕</sup> -NMe <sub>3</sub>	MeO <sup>-</sup>	MeOH	139
		4-R (R-Me, <i>t</i> -Bu)	MeO <sup>-</sup>	MeOH	22, 28, 120, 124, 144
		5-R (R-Me, <i>t</i> -Bu)	MeO <sup>-</sup>	MeOH	25
		6-R (R-Me, <i>t</i> -Bu)	MeO <sup>-</sup>	MeOH	25
		4-Cl	MeO <sup>-</sup>	MeOH	25
F	5	3-R (R-NH <sub>2</sub> , COO <sup>-</sup> , <i>t</i> -Bu, Me, MeO, COMe, F, Cl, Br, I, CF <sub>3</sub> , SO <sub>2</sub> Me, NO <sub>2</sub> )	MeO <sup>-</sup>	MeOH	124
			MeO <sup>-</sup>	MeOH	28
F	2,4		MeO <sup>-</sup>	MeOH	22, 70, 73, 121, 128, 139, 157, 159, 160
			MeO <sup>-</sup>	MeOH, MeOH-H <sub>2</sub> O	304
F	3,5		MeO <sup>-</sup>	dioxan	286
			MeO <sup>-</sup> + OH <sup>-</sup>	MeOH-H <sub>2</sub> O	176
			EtO <sup>-</sup>	EtOH	304
			EtO <sup>-</sup>	dioxan	286
			MeO <sup>-</sup>	MeOH	22
			MeO <sup>-</sup>	MeOH	{89, 125, 126, 132, 135, 136, 141, 142, 145, 146, 147, 319
Cl	2		MeO <sup>-</sup>	MeOH-H <sub>2</sub> O	304
			MeO <sup>-</sup>	dioxan	286
Cl	4		EtO <sup>-</sup>	dioxan	286
			MeO <sup>-</sup>	MeOH	{53, 70, 119, 123, 125, 128, 132, 136, 140, 141, 152

(continued)

TABLE 10. (continued)

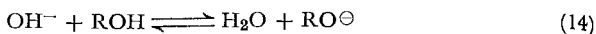
X	Position NO <sub>2</sub>	Substituent	Reagent	Solvent	Ref.
Cl	2	4-R	MeO <sup>-</sup>	dioxan	286
			EtO <sup>-</sup>	EtOH	18
			EtO <sup>-</sup>	dioxan	286
			MeO <sup>-</sup>	MeOH-benzene	143
Cl	4	4-R	MeO <sup>-</sup>	MeOH	{ 53, 119, 123, 125, 126, 134, 135, 136, 138, 141, 142, 145, 146, 147, 319, 320 }
			MeO <sup>-</sup>	MeOH	89
			MeO <sup>-</sup>	MeOH	119, 123, 124, 125, 136, 137, 141
			MeO <sup>-</sup>	MeOH	{ 54, 55, 70, 86, 119, 121, 123, 128, 129, 141, 143, 144, 190, 319, 321 }
Cl	2,4		MeO <sup>-</sup>	MeOH	24, 322
				MeOH-H <sub>2</sub> O	55
				60% aq. dioxan	129
				MeOH-methyl acetate	286
			MeO <sup>-</sup>	dioxan	141
				MeOH-dioxan	303
				MeOH-DMSO	286
				dioxan	299
			EtO <sup>-</sup>	EtOH	55, 71
			EtOH	60% dioxan-H <sub>2</sub> O	55, 121, 137
			PhO <sup>-</sup>	MeOH	169
			phenol, subst. phenols, <i>t</i> -BuOH	DMSO	

		naphthol, $\text{PhCH}_2\text{OH}$ , $(\text{CH}_3\text{OH})_2$ subst. phenols	aq. dioxan MeOH-DMSO	323 303
	5-R	$\text{MeO}^-$	MeOH	86, 120, 144
	6-R	$\text{MeO}^-$	MeOH	123, 136, 141
	Cl 2,6	$\text{MeO}^-$	MeOH	119, 123, 126, 141, 144, 190
		$\text{EtO}^-$	EtOH	21
	4-R	$\text{MeO}^-$	MeOH	21, 54, 119, 123, 126, 128, 129, 136, 138, 141, 144
	Cl 2,4,6	$\text{MeO}^-$	MeOH	23, 152
		MeOH, EtOH	MeOH	299, 324
		$\text{PhO}^-$	MeOH	325
		subst. phenols	MeOH	325
	Br 2	$\text{MeO}^-$	MeOH	132
		$\text{EtO}^-$	EtOH	190
	Br 4	$\text{EtO}^-$	EtOH	18, 190
		$\text{MeO}^-$	MeOH	128, 132
	Br 2,4	$\text{MeO}^-$	MeOH	70, 121, 128
		$\text{EtO}^-$	EtOH	190
		ROH/OH $^-$	ROH-H $_2$ O	162
	5-Me	KOH	MeOH	234
		$\text{MeO}^-$	MeOH	132, 145
	I 2	$\text{EtO}^-$	EtOH	18
	I 4	$\text{MeO}^-$	MeOH	128, 132, 152, 160
		$\text{PhO}^-$	MeOH	100
			DMF	100
	I 2,4	$\text{MeO}^-$	MeOH	70, 121, 128, 145, 151, 159, 160

R = alkyl.



In alcoholic solvents complications may arise through the equilibrium shown in equation 14.

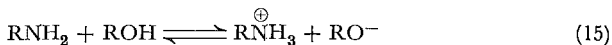


Because the alkoxy anion is a much stronger nucleophile than the hydroxyl ion, even small concentrations can lead to appreciable amounts of nitroaromatic ethers, beside the normal phenolic products. With sufficiently aqueous alcoholic solutions this danger can be suppressed. Highly reactive halides, such as picric chloride are already hydrolyzed by water.

### 5. Displacement by alkoxy- and phenoxy-anions

Alkoxy anions are in general very reactive and have been used widely in kinetic and mechanistic investigations (Table 10, cf. also III).

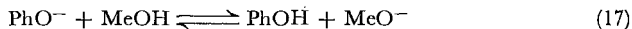
When dissolved in alcohol even such weak bases as amines may give a sufficient concentration of alkoxy anions, to effect some ether formation<sup>119</sup> (equation 15).



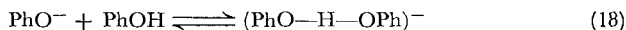
The apparent rate constant for displacement by phenoxide anion depends on the phenoxide ion concentration<sup>71</sup>. This has been explained by the partial consumption of phenoxide in the equilibria shown in equations 16–18.



and



or



Equilibrium (18) was suggested because it was found recently<sup>317</sup> that for *o*-methylphenoxide there was no dependence of the rate constant on the ion concentration.

### 6. Halogen exchange

Exchange of chlorine by fluoride in dipolar aprotic solvents like dimethyl sulfoxide or dimethylformamide is a reaction of preparative value for the synthesis of aromatic nitrofluoro compounds<sup>326</sup>. [In Table 11 a collection of these types of reactions is presented.]

In several instances halogen exchange in halonitroaromatics is accompanied by disturbing side reactions<sup>27,101,150,327</sup>.

TABLE 11. Nucleophilic displacement of halogen from nitrohalobenzenes by halogens.  
R = H, unless stated otherwise.

X	Positions of NO <sub>2</sub> group	Substituent on aromatic ring	Reagent	Solvent	Ref.
F	2,4		Br <sup>-</sup>		153
			NaI	acetone	27
			KI	acetone	327
Cl	2	6-Me	KI	acetone	327
			KF	DMF, DMSO	326
		4-R <sup>a</sup>	KF	DMF	326
		3,5-Cl <sub>2</sub>	KF	DMF	326
		5,6-Cl <sub>2</sub>	KF	DMF	326
Cl	4	5-Cl	KF	DMF	326
			KF	DMSO	326
		2-CF <sub>3</sub>	KF	DMF	326
		2,5-Cl <sub>2</sub>	KF	DMF	326
			KF	DMSO	169
Cl	2,4		KF	several, aprotic	326
			NaI; KI	acetone; DMF	27, 327, 328
		6-R	KI	acetone	327
Cl	2,4,6		LiCl, NaI, LiI	acetone	27
Br	2,4		KI; LiI	MeOH, acetone	150, 153, 331
		6-R	KI	acetone	331
			KI	acetone	332
		4-R	KI	acetone	332
			<sup>131</sup> I <sup>-</sup>	acetonitrile	280
I	2		<sup>131</sup> I <sup>-</sup>	acetonitrile	280
I	3		<sup>131</sup> I <sup>-</sup>	acetonitrile	280
I	4		<sup>131</sup> I <sup>-</sup>	acetonitrile	280
I	2,4		Br <sup>-</sup>	MeOH, acetone	150, 153
I	2,4		<sup>131</sup> I <sup>-</sup>	DMF	328

<sup>a</sup> R = alkyl

In dry acetone solution picryl chloride reacts with iodides giving trinitrobenzene, molecular iodine and mesityloxide<sup>27</sup>. It is thought that exchange does take place, but that the picryl iodide is reduced to the picryl anion which picks up a proton from acetone. The resulting carbanion reacts further with the acetone to give mesityloxide. In the presence of chloride instead of iodide anions this condensation does not take place. Sodium iodide does not react

with 2,4-dinitrochlorobenzene, but with 2,4-dinitrofluorobenzene it forms iodine and a number of unidentified products<sup>27</sup>.

The exchange of iodine in nitroiodobenzenes with radioactive iodide<sup>131</sup>I in acetonitrile can be effected at temperatures from 170–238°<sup>280</sup>. A recent survey of these and similar<sup>329,330</sup> halogen exchanges is given by Kendall and Miller<sup>328</sup>.

TABLE 12. Nucleophilic displacement of halogen from nitrohalobenzenes by sulfides.



X	Position of NO <sub>2</sub> group	Substituent on aromatic ring	Reagent	Solvent	Ref.
F	4	—	MeS <sup>-</sup>	MeOH	153, 156, 160
		—	PhS <sup>-</sup>	MeOH	23, 70, 73, 160
		—	PhCH <sub>2</sub> S <sup>-</sup>	several	303
		2-Me	PhS <sup>-</sup>	MeOH	73
		2-Br	PhS <sup>-</sup>	MeOH	73
F	2,4		MeS <sup>-</sup>	MeOH	133, 156, 160
			PhS <sup>-</sup>	MeOH	70, 73, 159, 160
Cl	2		MeS <sup>-</sup>	MeOH	155
			PhS <sup>-</sup>	dioxan-H <sub>2</sub> O	61
		4-R <sup>a</sup>	MeS <sup>-</sup>	MeOH	155
		4-R	PhS <sup>-</sup>	dioxan-H <sub>2</sub> O	55, 61
		5-R	PhS <sup>-</sup>	MeOH	49
		4-R <sup>a</sup>	PhS <sup>-</sup>	MeOH	49
		6-R	PhS <sup>-</sup>	MeOH	49
Cl	4		PhS <sup>-</sup>	dioxan-H <sub>2</sub> O	61
				MeOH	70
Cl	2,4		MeS <sup>-</sup>	MeOH	155, 159
			PhS <sup>-</sup>	MeOH	70
				60% aq. dioxan	55
				ROH <sup>a</sup> and ROH-H <sub>2</sub> O	304, 322
Br	2,4		PhS <sup>-</sup>	MeOH	70
I	4		MeS <sup>-</sup>	MeOH	153, 156
			PhS <sup>-</sup>	MeOH	100, 160
				DMF	100
I	2,4		PhS <sup>-</sup>	MeOH	70, 159, 160
			MeS <sup>-</sup>	MeOH	153, 156, 159, 160

<sup>a</sup> R = alkyl

## 7. Displacement by mercaptides

Though mercaptide and thiophenolate anions are weak bases, they are very strong nucleophiles and accordingly effective in halogen displacement.

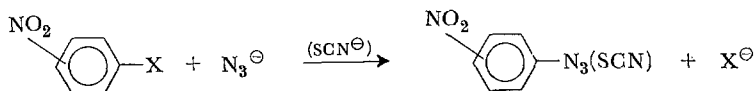
The nucleophilic properties and reactions are discussed in Section III.

Table 12 gives an account of recent literature on these reactions.

## 8. Displacement by azides and thiocyanate anions

These anionic reagents have nucleophilic reactivity, but are in general of minor importance<sup>333,334</sup>. A number of investigations has been carried out for studies on kinetics and mechanism (cf. Section III). The relevant reactions are collected in Table 13.

TABLE 13. Displacement of halogen from nitrohalobenzenes by azide and thiocyanate anions.



X	Position of NO <sub>2</sub> group	Substituent on aromatic ring	Reagent	Solvent	Ref.
F	4	—	NaN <sub>3</sub> , NEt <sub>4</sub> N <sub>3</sub> N <sub>3</sub> <sup>-</sup> N <sub>3</sub> <sup>-</sup>	several MeOH DMF	150 153, 160 149, 151
F	2,4		N <sub>3</sub> <sup>-</sup> SCN <sup>-</sup>	MeOH	159, 160 153
I	2	4-R <sup>a</sup>	N <sub>3</sub> <sup>-</sup> N <sub>3</sub> <sup>-</sup> ; SCN <sup>-</sup>	MeOH MeOH	145 145
I	4		N <sub>3</sub> <sup>-</sup>	MeOH, DMF, DMSO	150, 153, 160
I	2,4		N <sub>3</sub> <sup>-</sup> ; SCN <sup>-</sup>	MeOH	145, 160

<sup>a</sup> R = alkyl

## 9. Displacement by carbanions

Carbanions derived from compounds with 'active hydrogen' like malonic esters react as nucleophiles and displace halogen in halonitrobenzenes. The use of polar aprotic solvents such as DMF or DMSO is recommended for better yields<sup>288</sup>. In protic solvents the reaction is much less clean because of side reactions.

Grob and Weissbach<sup>335</sup> used successfully *t*-butanol as a solvent for reactions with *o*-chloronitrobenzene, which gave in solvents such as ether, ethanol, etc. very poor yields.

Formation of a Meisenheimer-type intermediate complex was studied by IR and UV-spectroscopy for the reaction of 2,4-dinitrofluorobenzene with diethyl malonate anion giving stable intermediates in DMF and DMSO<sup>336,337</sup>. Other reactions are collected in Table 14.

TABLE 14. Nucleophilic displacement of halogen from nitrohalobenzenes by carbanions.

$$\text{NO}_2\text{-C}_6\text{H}_4\text{-X} + {}^\ominus\text{CR}_1\text{R}_2\text{R}_3 \longrightarrow \text{NO}_2\text{-C}_6\text{H}_4\text{-CR}_1\text{R}_2\text{R}_3 + \text{X}^-$$

X	Position of NO <sub>2</sub> group	Substituent on aromatic ring	Reagent	Solvent	Ref.
F	2,4		CNCH <sub>2</sub> COOEt + NEt <sub>3</sub>		336, 337
			CH <sub>2</sub> (COOEt) <sub>2</sub> + NEt <sub>3</sub>		336, 337
Cl	2		CH <sub>2</sub> CNCOOEt	<i>t</i> -BuOH	335
			CH <sub>2</sub> (COOEt) <sub>2</sub>	<i>t</i> -BuOH	335
			<sup>⊖</sup> CH(COOEt)(COMe)	DMF	288
			<sup>⊖</sup> CH(COOEt) <sub>2</sub>	DMF	288
		4-R <sup>a</sup>	<sup>⊖</sup> CH(COOEt) <sub>2</sub>	DMF	288
		6-Cl	<sup>⊖</sup> CH(COOEt) <sub>2</sub>	DMF	288
			<sup>⊖</sup> CH(COOEt) <sub>2</sub>	<i>t</i> -BuOH	335
Cl	4		<sup>⊖</sup> CH(COOEt) <sub>2</sub>	aprotic solv.	288
		2-Cl	<sup>⊖</sup> CH(COOEt) <sub>2</sub>	DMF	288
	2,4,6		NEt <sub>3</sub> -acetone		226

<sup>a</sup> R = alkyl

## 10. Displacement by sulfite, carboxylate, thiosulfones, etc.

The sulfite ion is a nucleophilic reagent with a nucleophilic power comparable to alkoxides<sup>29</sup>.

The products formed in these reactions are sulphonates. The attacking species is thought to be trigonal SO<sub>3</sub><sup>2-</sup>. A high polarizability seems to be important in determining the nucleophilic

power<sup>69</sup>. (equation 19),

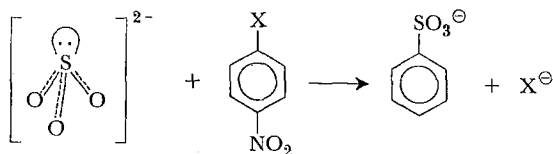


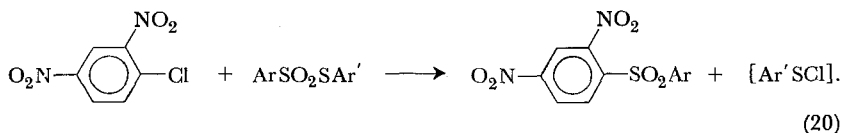
Table 15 gives a collection of reactions with sulfites and carboxylates.

TABLE 15. Displacement of halogen from nitrohalobenzenes by sulfite, carboxylate, thiosulfone, etc.

$$\text{NO}_2-\text{C}_6\text{H}_4-\text{X} + \text{Y}^- \longrightarrow \text{NO}_2-\text{C}_6\text{H}_4-\text{Y} + \text{X}^-$$

X	Position of NO <sub>2</sub> group	Reagent	Solvent	Ref.
F	2,4	SO <sub>3</sub> <sup>=</sup>	60% aq. EtOH	29
Cl	2,4	SO <sub>3</sub> <sup>=</sup>	60% aq. EtOH	29
		C <sub>6</sub> H <sub>5</sub> COOK	aq. dioxan	346
		<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> COOK	aq. dioxan	346
		<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COOK	aq. dioxan	346
Br	2,4	SO <sub>3</sub> <sup>=</sup>	aq. EtOH	29
I	2,4	SO <sub>3</sub> <sup>=</sup>	aq. EtOH	29

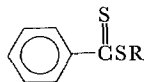
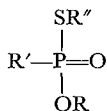
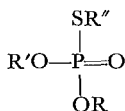
The use of diaryl-disulfides and their oxidation products with an SSO<sub>2</sub> group as reagents for nucleophilic displacement of halogen from activated aromatic systems has been studied extensively by Leandri and coworkers<sup>338-345</sup>. In this way nitro substituted diaryl sulfones can be obtained (equation 20):



The course of the reaction shows that hexavalent sulfur acts as the nucleophilic center.

## II. Reaction of nitrohalobenzenes with miscellaneous reagents.

Fluorine can be replaced by a mercapto group in 2,4-dinitrofluorobenzene by using<sup>347</sup> the following reagents:



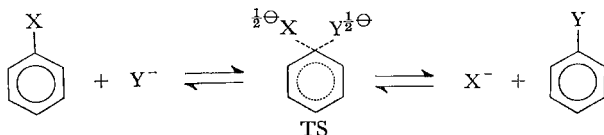
Other reagents used are hydrazine<sup>71</sup> (cf. section II.3) molten tetra-alkylammonium salts<sup>348,349</sup> and oximes<sup>350</sup>.

### III. KINETICS AND MECHANISM

#### I. Bond-making and bond-breaking as synchronous or non-synchronous processes

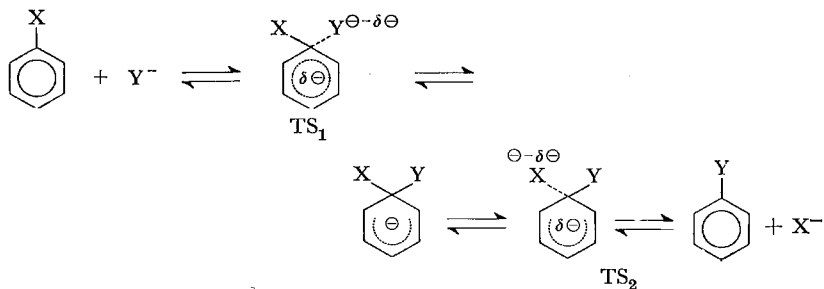
There has been some controversy as to what types of mechanism are operating in nucleophilic aromatic substitution<sup>4,79,81,82,87,99,174,175</sup>.

##### A. One stage:



and/or

##### B. Two stage:



Both cases are visualized in the energy profiles of figures 1 and 2.

In the one-stage process (Figure 1) C—X bond-breaking occurs synchronous with C—Y bond-formation and in the transition state (TS) both X and Y carry a fractional negative charge while weakly linked to the aromatic nucleus.

In the two-stage process (Figure 2) the C—X bond is hardly or not weakened; in reaching the first transition state (TS<sub>1</sub>) energy is consumed in altering the  $\pi$ -electron distribution in the aromatic ring and in changing the geometry at the carbon atom being attacked. A new  $\sigma$ -bond C—Y develops and a discrete cyclohexadienyl anion results as an intermediate. The 'aromatic'  $\pi$ -electron sextet is restored by expulsion of either X<sup>⊖</sup> or Y<sup>⊖</sup>, yielding the products or the

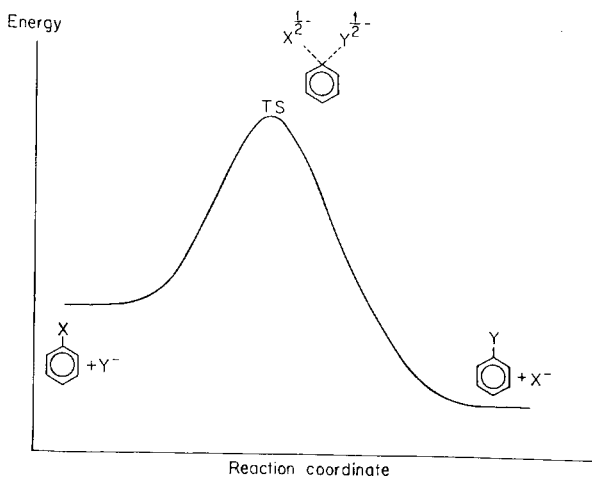


FIGURE 1. Course of a one-step nucleophilic displacement involving one transition state (TS).

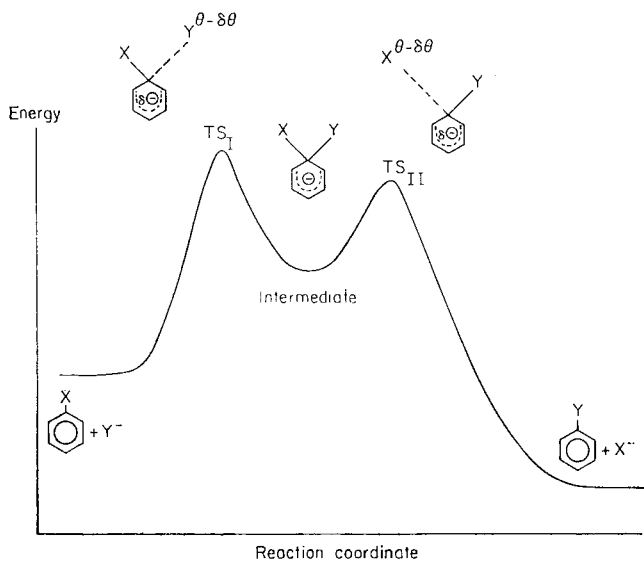


FIGURE 2. Course of a two-step nucleophilic displacement involving two transition states (TS<sub>I</sub> and TS<sub>II</sub>) and an intermediate  $\sigma$ -complex (Meisenheimer complex).



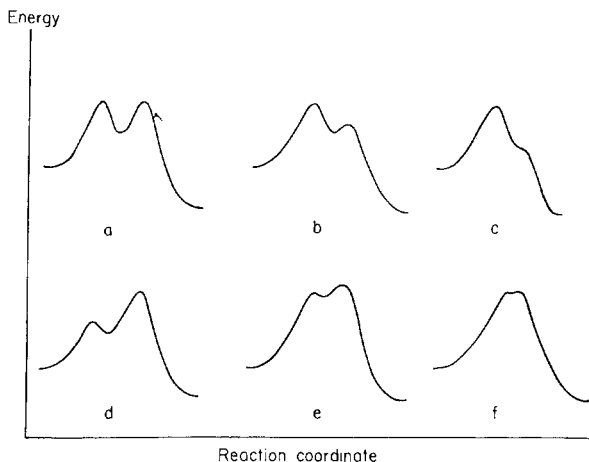


FIGURE 3. Relationships between energy and reaction coordinate for various types of aromatic nucleophilic substitution a.o. two-step processes (*a* and *b*) and one-step processes (*c* and *f*). Reactions *a*, *b* and *c* follow simple bimolecular kinetics; in reactions *d*, *e* and *f* the kinetics is more complicated by the rate-limiting second step.

starting materials. This two-step mechanism is generally accepted in textbooks although there is no rigid proof for its general applicability<sup>79,81,82,87,100,177,190,294,351</sup>. More realistically in most cases the true mechanism is somewhere between the extremes of the 'pure' one-stage and the 'pure' two-stage process (cf. also section III.4)<sup>98,174,175,294,323,346</sup>.

In Figure 3 a variety of such 'hybrid mechanism' is illustrated in diagrams which represent from left to right a gradual change from two-stage to one-stage character. As will be shown in the next sections many reactions e.g. most halogen displacements in halonitroaromatics follow a substitution pattern in which bond-making is a rate determining factor (Figure 3).

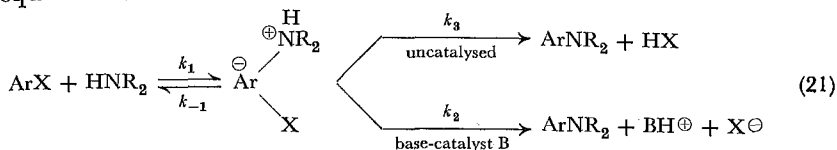
## 2. Kinetics of two-step displacement

The two-stage mechanism holds for many nucleophilic displacements and is supported by extensive kinetic (and other) investigations especially by Bunnett<sup>67,72</sup>, Miller<sup>153,156,159,160</sup> and many others (cf. Tables 1 and 2). There is ample evidence for the occurrence of (usually intensely colored) intermediate complexes. The mechanism of formation and decomposition of these (Meisenheimer) complexes and the relative importance of charge transfer complexes is still a subject of much dispute<sup>127,128,178-180,197,220,336,337,352-367</sup>. The

work of Gold and coworkers<sup>194-210</sup>, Foster and coworkers<sup>211-228</sup>, Ainscough and Caldin<sup>352-354</sup>, and Abe<sup>368-374</sup> is of particular importance. Only recently NMR-studies<sup>172, 204-210, 224, 303, 375-378</sup> have contributed to the elucidation of the structure of several complexes.

In this section we confine ourselves to some of the main conclusions derived from kinetic studies mostly, in order to understand why certain nucleophilic substitutions are promoted by catalysts and others are not.

With an intermediate of discrete life time the catalyzed and uncatalyzed reactions, e.g. with amines can be formulated as in equation 21.

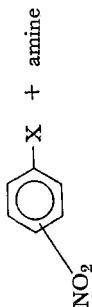


Depending on the relative magnitude of the various  $k$ -values, various types of kinetics can be distinguished.

When the final steps are relatively fast ( $k_2 + k_3(\text{B}) \gg k_{-1}$ ) the rate is expressed as  $v = k_1(\text{ArX})(\text{HNR}_2)$ , i.e. it has the same kinetic form as a common aliphatic  $\text{S}_{\text{N}}2$  reaction. This will correspond with energy profiles 3b and c (in section III.1). It applies generally to reactions with good leaving groups such as chlorine and bromine. Such reactions are insensitive to base catalysis because the frequency of reversion of the intermediate complex to reactants is low. Once the complex is formed, the leaving group X is rapidly split off and the overall-rate of displacement is exclusively determined by the rate of complex formation. Thus it is easy to understand that reactions of amines with 2,4-dinitrochloro- or bromobenzenes are insensitive to base catalysis.

On the other hand reversion becomes important<sup>78</sup> ( $k_{-1}$  relatively large) when the leaving group is *relatively* slow to separate from carbon (e.g. methoxy or phenoxy) and/or when the nucleophile (e.g. an amine) is easily expelled from the complex (diagrams 3d and 3e). The rate expression then becomes more complicated. When the concentration of the intermediate complex remains small during the reaction, steady state treatment is often applied and leads to an observed rate constant

$$k_A = \frac{k_1 k_2 + k_1 k_3(\text{B})}{k_{-1} + k_2 + k_3(\text{B})} \quad (22)$$

TABLE 16. Base catalysis on the displacement reactions of substituted nitrobenzenes with amines ( $k''/k'$  is a measure for base catalysis).

Substrate	Reagent	Solvent	Temp. °C	Observations	$k''/k'$	Ref.
1-F-4-NO <sub>2</sub>	piperidine	benzene	25	change of order from 1 to 2 in pip. <sup>b</sup>	≈90	91
	piperidine	benzonitrile	50	cat. <sup>a</sup> by pip. <sup>b</sup>	—	115
		methyl ethyl ketone	50	cat. by pip. <sup>b</sup>	—	115
		ethyl acetate	50	cat. by pip. <sup>b</sup>	—	115
1-F-2,4-(NO <sub>2</sub> ) <sub>2</sub>	<i>n</i> -BuNH <sub>2</sub>	MeOH	0		1.2	76, 293
	piperidine	benzene	25	change from 1st to 2nd order in pip. <sup>b</sup>	~1200	91
				cat. by MeOH	—	91
				α-pyridone	$k''$ : 3200	96
		benzene	25	pip. <sup>b</sup>	$k''$ : 600	96
				phenol	$k'$ : 220	96
				N(CH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub>	$k'$ : 32	96
				MeOH	$k''$ : 21	96
				pyridine	$k'$ : 2	96
				NEt <sub>3</sub>	$k'$ : 0	96
				<i>n</i> -methyl-α-pyridone	$k''$ : 0	96
				cat. by MeOH	~42	34, 35
				cat. by DABCO <sup>c</sup>	~64	34, 35

		cat. by pyr. <sup>d</sup>	~4	34, 35
		cat. by pip. <sup>b</sup> curved in presence of MeOH		35
		cat. by DMSO	~50	35
		no cat. by dioxan		35
		cat. by 2-Me-pip. <sup>b</sup>	~38	93
		cat. by 2,6-(Me) <sub>2</sub> -pip. <sup>b</sup>	~5.8	93
		cat. by benzylamine, non-linear	—	37
		cat. by pyr., <sup>d</sup> non-linear	—	37
		cat. by DABCO, <sup>c</sup> non-linear	—	37
		cat. by N-Me-benzylamine	600	37
		cat. by pyr. <sup>d</sup>	1.6	37
		DABCO <sup>c</sup>	630	37
		cat. by morpholine	982	40
		cat. by DABCO <sup>c</sup>	444	40
		cat. by pyr. <sup>d</sup>	58	40
		<i>k<sub>A</sub></i> decreases at high aniline conc. small salt effect	—	76, 293
		cat. by K-acetate	5 to 6	76, 293
		cat. by OH <sup>-</sup>	~2	76, 293
		no cat.	—	76, 293
		—	2.6	76, 293
		no cat.	—	382
		2nd order in aniline	—	382
		cat. by K-acetate	~150	72
		cat. by OH <sup>-</sup>	~350	72
2-Me-piperidine	benzene			
2,6-(Me) <sub>2</sub> -piperidine	benzene			
benzylamine	benzene			
		25		
		25		
		25		
N-Me-benzylamine	benzene			
		25		
morpholine	benzene			
		25		
aniline	MeOH			
		29.4		
aniline	60% dioxan-H <sub>2</sub> O			
aniline	<i>t</i> -BuOH			
aniline	ethanol			
	ethyl acetate			
N-Me-aniline	EtOH			
		29.4		
		35		
		35		
		67.2		

(continued)

TABLE 16. (*continued*)

Substrate	Reagent	Solvent	Temp. °C	Observations	$k'/k''$	Ref.
1-F-2,4,6-(NO <sub>2</sub> ) <sub>3</sub>	<i>p</i> -anisidine	60% dioxan-H <sub>2</sub> O	0	cat. by OH <sup>-</sup> , curve-linear	—	72
	aniline	benzene	25	acc. <sup>e</sup> by anisidine; pyr. <sup>d</sup> ; DABCO <sup>c</sup>	—	36
		ethanol	35	no cat.	—	382
1-Cl-2-NO <sub>2</sub>	piperidine	ethyl acetate	35	2nd order in aniline	—	382
		EtOH	100	cat. by pip. <sup>b</sup>	0.30	47
	piperidine	benzene	100	cat. by pip. <sup>b</sup>	0.10	47
1-Cl-2-NO <sub>2</sub> -4-CF <sub>3</sub>	piperidine	benzene	75	cat. by pip. <sup>b</sup>	0.15	50
	piperidine	benzene	25	cat. by pip. <sup>b</sup>	—	51
1-Cl-4-NO <sub>2</sub>	OH <sup>-</sup> NHMe <sub>2</sub>	16.7% dioxan-H <sub>2</sub> O	39	cat. by pip. <sup>b</sup>	28.9	50
		16.7% dioxan-H <sub>2</sub> O	39	no cat. by OH <sup>-</sup>	—	298
	piperidine	EtOH	100	no cat. by NHMe <sub>2</sub>	—	298
1-Cl-2,4-(NO <sub>2</sub> ) <sub>2</sub>	piperidine	benzene	100	no cat. by OH <sup>-</sup>	—	298
	piperidine	benzonitrile	50	cat. by pip. <sup>b</sup>	0.23	47
	piperidine	benzene	75	cat. by pip. <sup>b</sup>	2.4	47
	MeOM (M-Li, Na, K)	MeOH	25	slight cat. by pip. <sup>b</sup>	—	115
	allylamine			cat. by pip. <sup>b</sup>	7.00	50
				salt effect	—	321
	allylamine	chloroform	24.8	cat. by allylamine	4.60	102-111
			24.8	cat. by nitro compounds	—	102-111
	allylamine	EtOH	24.8	cat. by allylamine	0.36	102-111
		50% CHCl <sub>3</sub> -benzene	24.8	cat. by allylamine	3.3	102-111
		$\beta$ -phenylethanol	24.8	cat. by allylamine	0.89	102-111

$n$ -BuNH <sub>2</sub>	chloroform	24.8	cat. by hydrogen bond-forming comp. cat. by $n$ -BuNH <sub>2</sub> cat. by nitro comp. positive salt effects cat. by NEt <sub>3</sub> cat. by $n$ -BuNH <sub>2</sub> positive salt effect cat. by $n$ -BuNH <sub>2</sub> small salt effect;	— 2.59 — — 1.32 0.74 0.29	102-111 102-111 102-111 102-111 102-111 102-111 102-111 102-111
$t$ -BuNH <sub>2</sub>	DMF	24.8	no cat. by OH <sup>-</sup> cat. by $t$ -BuNH <sub>2</sub>	0.123	102-111
di- $n$ -Bu-amine	chloroform	24.8	cat. by $(n$ -Bu) <sub>2</sub> NH	0.21	102-111
	ethanol	24.8	cat. by $(n$ -Bu) <sub>2</sub> NH	0.53	102-111
$\beta$ -phenylethylamine	chloroform	24.8	cat. by PhCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	2.7	102-111
piperidine	ethanol	24.8	cat. by $(n$ -Bu) <sub>2</sub> NH	1.6	102-111
piperidine	benzene	25	no cat. by pip. <sup>b</sup> or $\alpha$ -pyridone	—	91, 96
piperidine	10% dioxan-H <sub>2</sub> O	29.4	slight cat. by OH <sup>-</sup>	—	78
piperidine	50% dioxan-H <sub>2</sub> O	0	no cat. by OH <sup>-</sup>	—	68
piperidine	benzene	25	MeOH retards	—	34
piperidine	benzene	25	accelerated by DMSO	—	38
piperidine	benzene	25	deceleration by phenol	—	96
2-Me-piperidine	benzene	25	no cat.	—	93
2,6-(Me) <sub>2</sub> -piperidine	benzene	25	no cat.	—	93, 94
aniline	50% dioxan-H <sub>2</sub> O	46	no cat. by OH <sup>-</sup>	—	68
$p$ -anisidine	benzene	25	acc. by anisidine; pyr. <sup>d</sup> ; DABCO <sup>e</sup>	—	36
pyridine	EtOH		slight cat. by pyr. <sup>d</sup> ; positive salt effect	—	102-111

(continued)

TABLE 16. (continued)

Substrate	Reagent	Solvent	Temp. °C	Observations	$k''/k'$	Ref.
1-Br-4-NO <sub>2</sub>	piperidine	benzonitrile	50	slight cat. by pip. <sup>b</sup>	—	115
1-Br-2,4-(NO <sub>2</sub> ) <sub>2</sub>	<i>n</i> -BuNH <sub>2</sub>	chloroform	24.8	cat. by <i>n</i> -BuNH <sub>2</sub>	2.33	107
	<i>t</i> -BuNH <sub>2</sub>	DMF	24.8	cat. by <i>t</i> -BuNH <sub>2</sub>	0.108	107
1-I-4-NO <sub>2</sub>	piperidine	benzonitrile	50	slight cat. by pip. <sup>b</sup>	—	115
1-I-2,4-(NO <sub>2</sub> ) <sub>2</sub>	<i>n</i> -BuNH <sub>2</sub>	chloroform	24.8	cat. by <i>n</i> -BuNH <sub>2</sub>	1.81	107
		DMF	24.8	no cat.	—	107
	<i>t</i> -Bu-NH <sub>2</sub>	DMF	24.8	no cat.	—	107
	piperidine	50% dioxan-H <sub>2</sub> O	0	no cat.	—	68
1-MeO-2,4-(NO <sub>2</sub> ) <sub>2</sub>	piperidine	10% dioxan-H <sub>2</sub> O	29.4	cat. by OH <sup>-</sup> , non-linear	—	78
	piperidine	MeOH		cat. by MeO <sup>-</sup>	—	78, 293
	piperidine	10% dioxan-H <sub>2</sub> O	29.4	cat. by OH <sup>-</sup> , non-linear	—	78
1-PhO-2,4-(NO <sub>2</sub> ) <sub>2</sub>	piperidine	60% dioxan-H <sub>2</sub> O	29.4	cat. by pip., <sup>b</sup> non-linear	—	78
				cat. by pip. <sup>b</sup>	53	78, 293
	piperidine	benzene	25	cat. by OH <sup>-</sup> , non-linear	—	78, 293
				2nd order in pip. <sup>b</sup>	high	92
				cat. by pyr. <sup>d</sup>	—	92
				MeOH, decrease of rate	—	92
	piperidine	60% dioxan-H <sub>2</sub> O	0	cat. by OH <sup>-</sup>	—	383
		60% dioxan-D <sub>2</sub> O	0	cat. by OH <sup>-</sup>	—	383
1-( <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O)-2,4-(NO <sub>2</sub> ) <sub>2</sub>	piperidine	50% dioxan-H <sub>2</sub> O	0	cat. by OH <sup>-</sup> (small)	—	68
		10% dioxan-H <sub>2</sub> O	29.4	cat. by OH <sup>-</sup> (small), non-linear	—	78
1-[2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O]-2,4-(NO <sub>2</sub> ) <sub>2</sub>	piperidine	10% dioxan-H <sub>2</sub> O	29.4	cat. by OH <sup>-</sup> (small), non-linear	—	78
1-SPh-2,4-(NO <sub>2</sub> ) <sub>2</sub>	piperidine	10% dioxan-H <sub>2</sub> O	29.4	cat. by OH <sup>-</sup> , curved	—	78
1-NHPh-2,4-(NO <sub>2</sub> ) <sub>2</sub>	NaOH	H <sub>2</sub> O		cat. by OH <sup>-</sup>	—	384

$1,4(\text{NO}_2)_2$	piperidine	benzonitrile	50	cat. by pip. <sup>b</sup>	—	115
$1\text{-SO}_2\text{Ph-2,4-(NO}_2)_2$	piperidine	50% dioxan- $\text{H}_2\text{O}$	50	slight cat. by pip. <sup>b</sup>	—	115
$1\text{-OPO}_3\text{-4-NO}_2$	piperidine	water	0	no cat. by $\text{OH}^-$	—	68
			39	cat. by pip. <sup>b</sup>	—	298
	$\text{NHMe}_2$	water	39	cat. by $\text{OH}^-$ , non-linear	—	298
				cat. by $\text{NHMe}_2$ , non-linear	—	298
	morpholine	water	39	cat. by $\text{OH}^-$ , non-linear	—	298
				cat. by $\text{OH}^-$	—	298

<sup>a</sup> cat. = catalysis.<sup>b</sup> pip. = piperidine.<sup>c</sup> DABCO = 1,4-diaza[2.2.2]bicyclooctane.<sup>d</sup> pyr. = pyridine.<sup>e</sup> acc. = acceleration.



With  $k_{-1} \gg k_2 + k_3(B)$  this simplifies to

$$k = {}_A \frac{k_1 k_2}{k_{-1}} + \frac{k_1 k_3}{k_{-1}} (B) = k' + k''(B) \quad (23)$$

Table 16 gives a survey of halogen displacements by amines, following this rate expression involving linear dependence of  $k_A$  on amine ( $B$ ) concentration. The ratio  $k''/k'$  is a measure of the catalytic activity, i.e. the relative magnitude of the accelerated and unaccelerated parts of the reaction at 1 mole base concentrations. In the intermediate case of a moderately good leaving group,  $k_{-1} > k_2 + k_3(B)$  will only hold for low base concentrations. Linear dependence of  $k_A$  on base concentration is then confined to a low base concentration region. At higher base concentrations the observed reaction constant  $k_A$  approaches asymptotically the value  $k_1$  i.e. the ultimate overall-rate is only governed by the rate of complex formation (as for good leaving groups in uncatalyzed reactions). A typical example of this so called 'curvilinear' dependence is given in

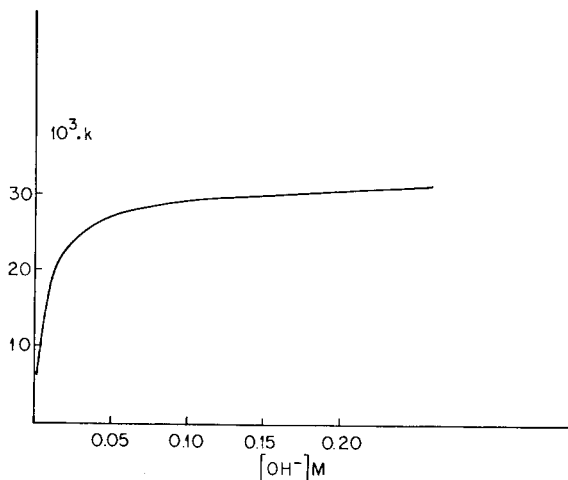
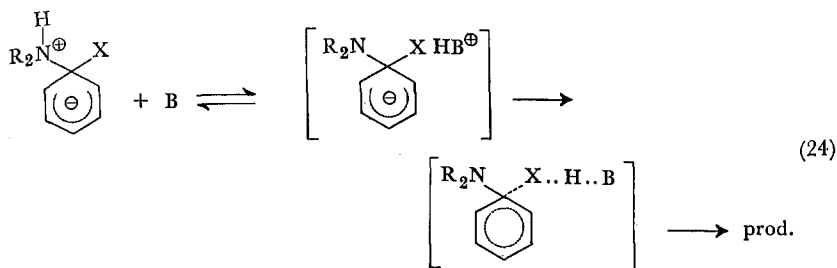


FIGURE 4. Reaction of 2,4-dinitrophenyl ether with piperidine catalyzed by  $NaOH^{78}$ .

in Figure 4 for the reaction of 2,4-dinitrophenyl ether with piperidine. Various mechanisms for base catalysis have been suggested:

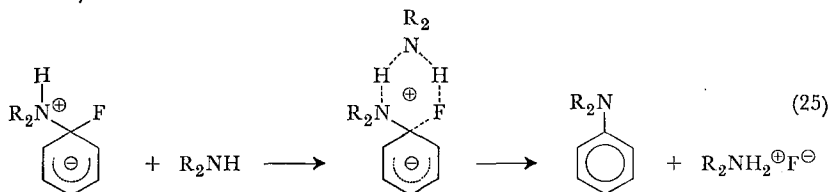
(i) Bunnett<sup>72,76-78</sup>, and Bernasconi and Zollinger<sup>34-36</sup> ascribe the action of a base  $B$  to proton removal from the intermediate ammonium complex followed by general acid catalysis by  $BH^+$  to

remove X, the latter step being *relatively* slow<sup>382</sup> (equation 24),

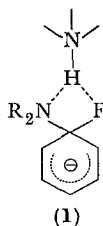


In some instances<sup>51,92,383</sup> a hydrogen isotope effect has been found indicating that N—H fission is an (unusual but not impossible) rate-determining factor (cf. section III.3).

(ii) For catalysis by a secondary amine (piperidine) a six-center transition state has been postulated<sup>11</sup> (cf. also reference 96) (equation 25).



(iii) For a tertiary amine this has been modified to a four-center intermediate<sup>113,30,79</sup> (cf. also reference 175)



For the neutral hydrolysis of fluoro compounds intramolecular hydrogen bonding is probably more important than for chloro compounds<sup>175</sup>. Similar cyclic transition states have been suggested in other cases<sup>30,79</sup>. Inspection of Table 16 shows that catalytic effects are more pronounced in nonpolar than in polar solvents<sup>34-40,115,116</sup>. Mechanistic conclusions based on small catalytic effects ( $k''/k' < 10$ ) must be considered with caution since these can equally well be

attributed to medium effects<sup>34,35,68,72,75-77,105,107</sup> (cf. also section III.3).

In several recent studies attention is directed to the details of the second step<sup>47,51,92,158,383</sup>.

### 3. Isotope effects

Generally the relative importance of bond-breaking and bond-making can be inferred<sup>15</sup> from isotope effects and this approach has contributed much to the understanding of *electrophilic* aromatic substitution. Unfortunately exact measurement of a hydrogen isotope effect in *nucleophilic* aromatic substitution is not possible because anionic hydrogen displacement is accompanied by side reactions which prevent accurate rate measurements. Although halogen displacement can be measured with much greater accuracy, isotope effects for halogens are too small to be measured (cf. reference 386).

TABLE 17. Isotope effects in nucleophilic aromatic substitution reactions.

Reaction	Isotope effect	Ref.
1-F-2,4-dinitrobenzene + <i>p</i> -anisidine in benzene	$k_H/k_D : 1.7$	15, 32
<i>p</i> -anisidine in pyridine	$k_H/k_D : —$	15
piperidine in benzene	$k_H/k_D : —$	91
2-Cl-nitrobenzene + piperidine in toluene	$k_H/k_D ; —$	284
piperidine in benzene	$k_D''/k_H'' : 1.27$	50
4-Cl-nitrobenzene + piperidine in toluene	$k_H/k_D : —$	284
piperidine in benzene	$k_D''/k_H'' : 1.12$	50
1-Cl-2,4-dinitrobenzene + <i>n</i> -butylamine in $\text{CHCl}_3$	$k_H/k_D : —$	108
<i>p</i> -anisidine	$k_H/k_D ; <1$	15, 32, 36
1-Cl-2-nitro-4-trifluoromethylbenzene + piperidine in benzene	$k_D''/k_H'' : 0.50$	56
	$k_H/k_D : 1.2$	51
1-C <sub>6</sub> H <sub>5</sub> O-2,4-dinitrobenzene + piperidine in benzene	$k_H/k_D : 1.27$	92
piperidine in 10% dioxan-H <sub>2</sub> O	$k_H/k_D : 1.46$	78
piperidine in 60% dioxan-H <sub>2</sub> O	$k_H/k_D : >1$	383
piperidine in 60% dioxan-H <sub>2</sub> O; $[\text{OH}^-] = 0.005$	$k^{16}\text{O}/k^{18}\text{O} : 1.0109$	383
$[\text{OH}^-] = 0.033$	1.0070	383
1-C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> -2,4-dinitrobenzene + piperidine in benzene	$k^{32}\text{S}/k^{34}\text{S} : 1.013$	385
2-Cl-5-nitropyridine + D <sub>2</sub> O	$k_H/k_D : 2.36$	387

A primary isotope effect of 0.5–1% has been reported for the reaction of piperidine with 2,4-dinitrophenylsulphone with  $^{32}\text{S}$  and  $^{34}\text{S}^{15,385}$ , indicating that C—S rupture is a rate determining factor.

By far the most isotopic studies have been carried out with deuterated amines. The reactions listed in Table 17 with no detectable isotope effect are characteristic for processes in which only the first step is rate determining (cf. section III.2). For a number of amine reactions however, a hydrogen isotope effect is observed and this means that N—H rupture occurs in the rate limiting step (cf. section III.2).

Interestingly Brieux *et al.*<sup>50</sup> have noticed an isotope effect for the reaction of *p*-nitrochlorobenzene with piperidine (only at sufficiently high concentration) whereas the effect is absent at all amine concentrations for *o*-nitrochlorobenzene. This is explained by an intramolecular hydrogen bond between N—H and the nitro group, which makes the *ortho*-compound relatively insensitive for base catalysis. Similar conclusions have been reached by Ross<sup>108,110</sup> and others<sup>51,87,92,383</sup>. These results support the mechanistic conclusions based on non-tracer kinetic experiments (section III.2).

In this connection also the work of Bunnett and coworkers<sup>67,27</sup> on the 'element effect' should be mentioned, which is formally equivalent to an isotope effect<sup>386</sup>. As can be seen from Table 27 (section III.7) the rate of reaction for the displacements 4 to 9 is almost independent on the nature of X, implying that the aryl-X bond is only broken after the rate-limiting step.

#### 4. The nature of intermediate complexes and transition states

Besides kinetics and isotope effects further support for the occurrence of an intermediate complex in nucleophilic aromatic substitution is derived from the observation of strong coloration developing rapidly upon admixture of most nitroaromatic substrates and a nucleophile. Such colors are characteristic for charge transfer and Meisenheimer complexes<sup>17,375–381</sup>.

Not all nucleophilic displacements proceed with color change. For instance it is absent in the reaction of iodide ion with 2,4-dinitrohalobenzenes<sup>327,331,332,351</sup> and this has been cited as an indication that no Meisenheimer type intermediates are involved<sup>174,175</sup>. In such a case bond-making and bond-breaking are supposed to be synchronous processes, as in  $S_N2$  reactions, albeit with a different

stereochemistry. To satisfy quantum mechanical principles for these synchronous processes Parker<sup>295</sup> suggested participation of 3d-orbitals, but a more sophisticated model avoiding high energy-d-orbitals was introduced by Simonetta<sup>190,191,193,388,389</sup>. In this model the substituent (X) to be displaced and the nucleophile (Y) are treated as one entity ('pseudo atom') in the activated complex. The atomic orbitals of X, Y and C<sub>(1)</sub> of the aromatic ring combine to molecular orbitals as depicted schematically in Figure 5. This is

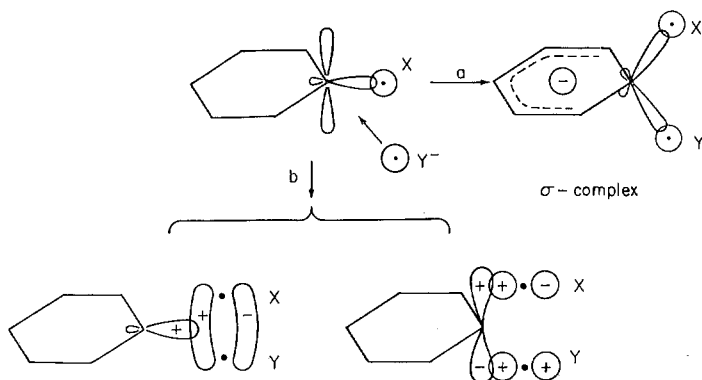


FIGURE 5. Orbitals involved in the attack of a nucleophile  $Y^-$  on an X-substituted aromatic molecule: (a) a  $\sigma$ -complex with  $sp^3$ -hybridisation is formed. (b) a quasi  $\sigma$ -bond and a quasi  $\pi$ -bond are formed with the pseudo-atom XY.

roughly analogous to a carbonyl double bond, with oxygen replaced by a pseudo atom XY, linked to the ring via a quasi  $\sigma$ -bond, symmetrical with respect to the plane of the ring and a quasi  $\pi$ -bond antisymmetrical with respect to this plane.

This description allows for a large degree of freedom in the stability and rigidity in the activated complex. Moreover the quasi  $\pi$ -bond introduces double bond character between the XY pseudo atom and the rest of the molecule. This makes it possible to spread charge over the  $\pi$ - as well as over the quasi- $\pi$  system which is promoted by electron withdrawing nitro groups in the benzene ring. Furthermore the  $\sigma$ -skeleton of the aromatic ring is not disturbed, nor is there generation of strain. This description is compatible with a synchronous one-stage<sup>190</sup> as well as with a two-stage mechanism. It has successfully been applied in the calculation of the  $\pi$ -electron energy in the transition state<sup>193</sup>.

Simonetta's model gives a reasonable explanation for one-stage

substitution processes in which Meisenheimer complexes are circumvented. Whether this model should also be applied to two-stage processes seems less certain.

At any rate there are many successful calculations (Valence bond and MO—LCAO) based on the classical Wheland model with a carbon atom at which substitution occurs via changes in hybridization from  $sp^2 \rightarrow sp^3 \rightarrow sp^2$  86,87,94,170,173,175,185,278,307,308,372,390. In the  $sp^3$  stage the aromatic  $\pi$ -electron sextet is broken up, but this is largely compensated for by the formation of a new  $\sigma$ -bond, and thus a relatively stable Meisenheimer complex results. Miller<sup>153</sup> calculated activation energies—in good agreement with experimental values—for such processes, taking into account bond energies, electron affinities, delocalization energies and solvation and desolvation energies.

In protic solvents the calculated order of reactivity with *p*-iodonitrobenzene was:



Similar calculations were made by Bunnett<sup>10</sup> and Hudson<sup>9</sup>, with further refinements by Miller and coworkers<sup>159,160</sup>.

Rates of displacement have furthermore been related to Brönstedt relationships<sup>9,90,113,167,173</sup> (cf. in particular reference 175 and references therein).

In recent years activated complexes have been studied by the measurement of activation volumes  $\Delta V^*$  obtained from the variation of reaction rates with pressure (equation 26),

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\Delta V^*/RT. \quad (26)$$

For the reaction of 2,4-dinitrochlorobenzene with *n*- and *t*-butylamine in ethanol a 3 to 7-fold rate increase was observed at a pressure increase of 1000 kg/cm<sup>2</sup> 300,301. This means that  $\Delta V^*$  is negative and that the transition state is more compact than the initial stage. This can be partly attributed to a considerable degree of new bond formation in a tight transition state (implying that bond making is the chief rate determining factor).

In the reaction of amines, bond making involves development of charges so that (polar) solvent molecules are attracted in the transition state, more than in their initial stage with neutral molecules ( $\Delta V^*$  negative). This also tends to make  $\Delta V^*$  negative. In the reaction of hydroxyl ion with 2,4-dinitrofluorobenzene the pressure effect is

TABLE 18. Sensitivity of nucleophilic displacement of halogen from halonitrobenzenes to substituent (Z) variation as expressed by the Hammett  $\rho$ -value ( $n$  = number of Z-substituted compounds;  $r$  = correlation coefficient).<sup>a</sup>

Aromatic substrate	Reagent	Solvent	Temp. °C	$n$	$\rho$	$r$	Ref.
1-F-4-Z	MeO <sup>-</sup>	MeOH	50	3	+7.55	—	144
1-F-3-Z-5-NO <sub>2</sub>	MeO <sup>-</sup>	MeOH	100	12	+5.28	0.997	28
1-F-4-Z-2-NO <sub>2</sub>	EtO <sup>-</sup>	EtOH	49.6	7	+4.071	0.994	20, 393
1-Cl-4-Z	MeO <sup>-</sup>	MeOH	50	4	+8.47	—	152
1-Cl-4-Z-2-NO <sub>2</sub>	MeO <sup>-</sup>	MeOH	25	7	+3.941	0.984	53, 54, 393
1-Cl-4-Z-2-NO <sub>2</sub>	MeO <sup>-</sup>	MeOH	50	5	+3.897	—	145
1-Cl-4-Z-2-NO <sub>2</sub>	MeS <sup>-</sup>	MeOH	0	2	+3.60	—	155
1-Cl-4-Z-2-NO <sub>2</sub>	PhS <sup>-</sup>	60% dioxan-H <sub>2</sub> O	25.35	3	+4.5	—	61
1-Cl-4-Z-2-NO <sub>2</sub>	piperidine	benzene	45	14	+4.08	0.992	45
1-Cl-4-Z-2-NO <sub>2</sub>	piperidine	benzene	45	26	+3.80	0.934	45
1-Cl-5-Z-2-NO <sub>2</sub>	piperidine	benzene	45	12	+2.63	0.893	45
1-Cl-5-Z-2-NO <sub>2</sub>	PhS <sup>-</sup>	MeOH	35	8	+5.15	0.995	49
1-Cl-5-Z-2-NO <sub>2</sub>	piperidine	benzene	45	8	+3.71	0.995	49
1-Cl-5-Z-2-NO <sub>2</sub>	piperidine	MeOH	80	8	+3.03	0.991	49, 297
1-Cl-6-Z-2-NO <sub>2</sub>	PhS <sup>-</sup>	MeOH	35	7	+3.46	0.975	49
1-Cl-6-Z-2-NO <sub>2</sub>	piperidine	benzene	75	7	+2.65	0.991	48
1-Br-4-Z-2-NO <sub>2</sub>	piperidine	piperidine	25	10	+4.918	0.973	308, 393
			35	10	+4.865	0.973	
	piperidine	benzene	110	7	+4.82	—	311
1-I-4-Z-2-NO <sub>2</sub>	MeO <sup>-</sup>	MeOH	50	2	+3.87	—	145
	N <sub>3</sub> <sup>-</sup>	MeOH	50	4	+3.12	—	145
	SCN <sup>-</sup>	MeOH	50	4	+5.05	—	145
1-Cl-4-Z-2,6-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup>	MeOH	45	5	+4.3	—	54
1-Cl-5-Z-2,4-(NO <sub>2</sub> ) <sub>2</sub>							
( $\sigma_m$ -normal <sup>b</sup> )	MeO <sup>-</sup>	MeOH	50	7	+5.8 <sup>b</sup>	low	144
( $\sigma_m$ -amended)	MeO <sup>-</sup>	MeOH	50	7	+3.676 <sup>c</sup>	0.999	144

<sup>a</sup> For a compilation of substituents (Z), generally used in determining Hammett relationships see references 393 and 404-406.<sup>b</sup> Calculated with  $\sigma_m$ -normal<sup>b</sup>.<sup>c</sup> Calculated with  $\sigma_m$ -amended.

TABLE 19. The relative order of activating power of halogen atoms X on the displacement of other halogen atoms.

Reaction:	Activating influence							Ref.
	I	Br	>	Cl	>	F	H	
4-X-2-NO <sub>2</sub> -fluorobenzene + EtO <sup>-</sup> in EtOH	I 16.8	Br 17.0	>	Cl 11.6	>	F 1.68	H 1.00	20
3-X-5-NO <sub>2</sub> -fluorobenzene + MeO <sup>-</sup> in MeOH	Br 118	Cl 86.9	>	I 75.0	>	F 55.4	H 1.00	28
5-X-2-NO <sub>2</sub> -chlorobenzene + PhS <sup>-</sup> in MeOH	Br 179	I 163	>	Cl 121	>		H 1.00	49
4-X-2-NO <sub>2</sub> -chlorobenzene + MeO <sup>-</sup> in MeOH	I 17.4	Br 15.4	>	Cl 14.0	>	F 0.90	H 1.00	124
4-X-2-NO <sub>2</sub> -chlorobenzene + piperidine in benzene	I 12.1	Br 9.6	>	Cl 6.2	>		H 1.00	45
5-X-2-NO <sub>2</sub> -chlorobenzene + piperidine in benzene	Br 34.5	Cl 32.3	>	I 24.9	>		H 1.00	45, 297
4-X-2-NO <sub>2</sub> -bromobenzene + piperidine in piperidine	Br 7.83	Cl 5.58	>	I 5.41	>	F 2.60	H 1.00	308



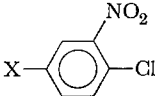
negligible<sup>176</sup>. This has been taken as evidence for a 'loose' transition state, where bond formation has made little progress.

However, such conclusions must be taken with reservation since the degree of solvation e.g. for the charged nucleophile ( $\text{OH}^-$ ) is a factor of great uncertainty. It is beyond the scope of this chapter to discuss related investigations in detail<sup>180, 302, 391, 392</sup>.

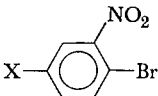
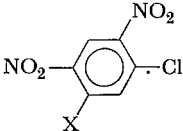
## 5. Effect of substituents in the substrate

Nucleophilic aromatic substitution requires a nitro group or another strong electron attracting group to create centres of low


TABLE 20. Activation by group X on the displacement of halogen from *o*-halonitrobenzenes by methoxide ions in methanol.

					
X	$k_{\text{rel}}, 50^\circ$ <sup>146</sup>	X	$k_{\text{rel}}, 50^\circ$ <sup>135, 142</sup>	X	$k_{\text{rel}}, 50^\circ$ <sup>147</sup>
H	1.00	H	1.00	H	1.00
$-\text{N}_3$	2.41	$-\text{SO}_3^-$	5.44	$-\text{SMc}$	21.7
$-\text{N}=\text{N}(\text{Ph})\text{O}^\oplus$	$5.35 \times 10^2$	$-\text{SO}_2\text{NH}^-$	$2.60 \times 10$	$-\text{NMe}_3^\oplus$	$2.13 \times 10^4$
$-\text{N}=\text{NPh}$	$1.07 \times 10^3$	$-\text{SO}_2\text{NC}_5\text{H}_{10}$	$6.09 \times 10^3$		
$-\text{N}(\text{O})=\text{NPh}^\oplus$	$3.31 \times 10^3$	$-\text{SO}_2\text{NMc}_2$	$7.57 \times 10^3$	$-\text{S}^\oplus\text{Me}_2$	$3.16 \times 10^5$
$-\text{Ac}$	$8.08 \times 10^3$	$-\text{SO}_2\text{NMcPh}$	$8.14 \times 10^3$		
$-\text{CHO}$	$2.02 \times 10^4$	$-\text{SO}_2\text{Me}$	$12.8 \times 10^3$	Me	$0.119^{287}$
$-\text{CN}$	$3.81 \times 10^4$			$\text{CF}_3$	$815^{287}$
$-\text{NO}_2$	$6.73 \times 10^5$				
$-\text{NO}$	$5.22 \times 10^6$				
$-\text{N}=\text{N}^\oplus$	$3.83 \times 10^8$				

 			
X	$k_{\text{rel}}, 50^\circ$ <sup>139</sup>	X	$k_{\text{rel}}, 100.8^\circ$ <sup>120</sup>
H	1.00	$-\text{O}^-$	$1.26 \times 10^{-4}$
$\text{NMe}_3^\oplus$	$1.43 \times 10^4$	$\text{NMe}_2$	$1.97 \times 10^{-2}$
$\text{NO}_2$	$1.01 \times 10^5$	Me	$3.85 \times 10^{-1}$
		MeO	$7.45 \times 10^{-1}$
		H	1.00
		Cl	13.3

electron density for attack by the nucleophile. This type of activation is quantitatively expressed by *high positive*  $\rho$ -values in the Hammett equation  $\log k_R/k_H = \sigma_{RP}$ . Table 18 shows that  $\rho$ -values range from +2.6 to +8.4. In many reaction series the Hammett relation is followed almost perfectly i.e. correlation coefficients<sup>393</sup> approach unity. When an electron donating substituent enters into mesomeric interaction with an *ortho*- or *para*-nitro group, deviations from linearity are observed which are reflected in a lower correlation coefficient as shown in particular by the recent studies of Brioux and coworkers<sup>48,49</sup>. The  $\sigma$ -values of halogens are of little use in predicting the rate of displacement of another halogen (in dihalonitro aromatics). The irregularity (Table 19) is caused by the interplay<sup>20,124</sup> of inductive effects ( $F > Cl > Br > J$ ), inductomeric effects ( $J > Br > Cl > F$ ) and mesomeric effects ( $F > Cl > Br > J$ ). In 2-nitrohalobenzenes halogen displacement can be strongly promoted by introduction of a second electron attracting substituent in the 4-position. The data in Table 20 show that an extra nitro group increases the rate more than 100000-fold and this activating power is surpassed only by the nitroso- and the diazonium groups. Various substituents with a carbonyl group have separately been collected in Table 21. The interesting point is that all COX-groups promote displacement but when placed in *ortho*-position to chlorine there are some exceptions. The deactivating effect of a carboxylate group in

  
 TABLE 21. The influence of a  $-\text{C}(=\text{O})\text{X}$  group on the displacement of chlorine by methoxide ions in methanol.

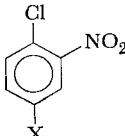
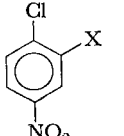
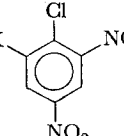
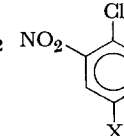
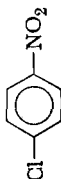
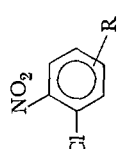
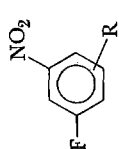
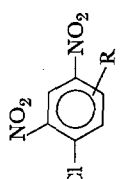
	 50° 126,141	 50° 126,141	 0° 141	 0° 131,141
X = H	1.00	1.00	1.00	1.00
COO <sup>-</sup>	7.12	0.373	0.007	11.5
CONH <sub>2</sub>	262	462	27.9	240
CONMe <sub>2</sub>	380		0.188	65
CONHPh		1700		
COOMe	1560	174	5.55	728
COMe	1990	246		
CHO	2240	284		
COPh	2655	21.6	0.615	820

TABLE 22. Deactivation factors ( $k_H/k_R$  resp.  $k_H/k_{OR}$ ) of halogen displacements.

Substrate	R or OR	$k_H/k_R$ resp. $k_H/k_{OR}$					Reagent and reference
		Position of R with respect to halogen (= pos 1)					
		2	3	4	5	6	
	Me	>1	4.65				
	MeO	2.4	1.19				
	EtO	4.0	4.03				
	Me		64.4	5.13	1.01	140	piperidine in MeOH at 100° 43.44
	MeO		33.4	21.7	0.30	5.12	
	EtO		80.0	25.8	0.43	6.34	
	Me			10.2	2.5	10.6	MeO <sup>-</sup> in MeOH at 130.4° 25
	<i>t</i> -Bu			52.0	3.3	9.45	
	Me		970		3.62	276	{piperidine in methanol at 20°
	Me		3400		42.9	13.5	MeO <sup>-</sup> in MeOH at 20°
	<i>t</i> -Bu		—		57.7	—	piperidine in MeOH at 90° 89

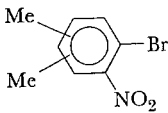
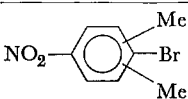
Chemical Structure	Substituent	EtO <sup>-</sup> in EtOH <sup>21</sup>		KI in acetone at 80° <sup>332</sup>	piperidine in benzene at 78° <sup>281</sup>
		Me	<i>t</i> -Bu		
		5.67	3.23	8.13	133
		6.32		6.32	1.14
	Me	114		4.97	133
	Me	33	3.16		

position 6 of 2,4-dinitrochlorobenzene is particularly large ( $k_{\text{COO-}}/k_{\text{H}} = 0.007$ ). Apart from some steric effect this has been attributed to the repulsive field effect exerted by the negative carboxylate group on the approaching methoxide ion<sup>59</sup>.

Nucleophilic displacement is disturbed in the presence of activating groups, which are themselves vulnerable to nucleophilic attack, e.g. the aldehyde group. In order to minimize such side reactions<sup>126</sup> in favor of normal halogen displacement, Miller<sup>145</sup> has selected the mildly nucleophilic  $\text{SCN}^\ominus$  ion in determining the (extra) activating effect of various vulnerable groups in the 4-position of 2-nitroiodobenzenes. J. Miller and coworkers published an extensive series of papers on the influence of substituent effects on nucleophilic displacement from aromatic nitro compounds<sup>119-161</sup>.

As expected, deactivation of nucleophilic displacement is effected by electron donating alkyl and alkoxy substituents (Table 22). Two methyl groups (Table 23) in *o*- and *p*-nitrobenzenes have almost a

TABLE 23. The relative reactivities of dimethylsubstituted 1,2- and 1,4-bromonitrobenzenes with piperidine in boiling benzene<sup>281</sup>.

	$k_{\text{H}}/k_{(\text{Me})_2}$				
Positions of methyl groups	3,5	3,6	4,5	4,6	5,6
	93,5	—	6,1	530	133
Positions of methyl groups	2,3	2,5	2,6	3,5	3,6
	395	113	1975	264	

2000-fold rate lowering effect when both are flanking the halogen atom. This and certain reactions from Table 22 illustrate the importance of steric factors, also dominant in many other reactions as shown in the next section.

## 6. Steric effects

Various types of steric effects on nucleophilic aromatic substitution can be distinguished<sup>1,4,49,89,101,125,126,132,295</sup>. The activating electron-withdrawing power of the nitro group is largest when it is coplanar with the aromatic ring, a condition for optimum mesomeric interaction. *Ortho*-substituents may prevent coplanarity and

thus lower displacement rates<sup>49</sup>, as shown in Table 24. Many *o*-nitrohalobenzenes are therefore less reactive than the *para*-isomers towards nucleophilic reagents.

TABLE 24. Effect of size and position of an alkyl substituent on the dechlorination of 2,4-dinitrochlorobenzene. Reaction with piperidine in EtOH.

$k_{rel}$ 187	13.7	3.34	1.00

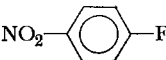
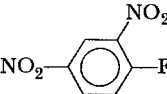
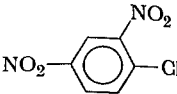
Steric influences seem to be particularly prominent when the leaving group is flanked at both sides by substituents while there is also a strong decrease in activating power when both *ortho*-positions to a nitro group are substituted<sup>25,43,44,89,90,119,123,132,281</sup>. An illustration is given in Table 24. Also the iododebromination studied by Fierens and Halleux<sup>331</sup> is susceptible to steric hindrance of alkyl groups, as can be seen from Table 25 (cf. also reference 123). For an

TABLE 25. Influence of an alkyl group on the rate of replacement of bromine by iodine.

 $\text{NO}_2$ -C <sub>6</sub> H <sub>3</sub> (Br)(R) + KI in dry acetone at 80°.					
R:	H	Me	Et	<i>i</i> -Pr	<i>t</i> -Bu
$10^6 \cdot k_2$	2800	620	360	430	4.8

unhindered approach of the nucleophile it is of course important that the nucleophilic centre is not shielded too much by bulky groups. For aliphatic amines steric factors are the most important in determining reactivities<sup>29,72,114,116,117,294,295,307</sup>. For instance 2,6-dimethylpiperidine is about 200000 times less reactive than piperidine in displacing halogen from 2,4-dinitrofluoro- and chlorobenzenes<sup>94</sup>. This effect is further demonstrated in Table 26 for some piperidines<sup>94,95</sup>. An *ortho*-nitro group does not enhance appreciably the relative difference in halogen displacement rates by piperidine and substituted piperidines. Suhr<sup>114</sup> came to the same conclusion of only a small steric interaction of the *ortho*-nitro group. In pentachloronitrobenzene steric congestion changes the nitro group from an activating to an activated group, which is displaced by sodium

TABLE 26. Influence of the introduction of methyl substituents in the 2- and 6-positions of piperidine on its rate of reaction in halogen displacement<sup>94,95</sup>.

	 DMSO, 25° $k_{\text{rel.}}$	 PhH, 25° $k_{\text{rel.}}$	 PhH, 25° $k_{\text{rel.}}$
piperidine	14,500	59,700	214,000
2-methylpiperidine	26	228	101
<i>trans</i> -2,6-dimethylpiperidine	1	1	1
<i>cis</i> -2,6-dimethylpiperidine			0.16

methylate, in preference to any of the chlorine atoms<sup>394</sup> (cf. also section IV).

Steric effects in nitrohalonaphthalenes are discussed in section V.

## 7. Reactivity of halogens and comparison with other leaving groups

A glance at the various types of energy profiles (section III.1) and the corresponding kinetic expressions (section III.2) shows that a general prediction of the order of halogen reactivity in nucleophilic aromatic substitution is impossible<sup>85,152,160,164,395</sup>. The simplest kinetics are found for reactions with good leaving groups (Tables 27 and 27a), when product formation is governed exclusively by the rate of complex formation (cf. section III.2).

The high reaction rate of 2,4-dinitrofluorobenzene (Sanger's reagent for amino acids) with piperidine is caused by the large

TABLE 27. Relative rates of the reaction of 1-X-2,4-dinitrobenzenes with piperidine in MeOH at 0°<sup>67</sup>.

X	$k_{\text{rel.}}$
F	3300
NO <sub>2</sub>	890
OSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	100
SOC <sub>6</sub> H <sub>5</sub>	4.7
Br	4.3
Cl	4.3
SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3.2
OC <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> - <i>p</i>	3.0
I	1.0

TABLE 27a. Relative leaving abilities for various substituents X in the reaction

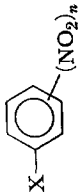


X	$k_{\text{rel}}$	X	$k_{\text{rel}}$	X	$k_{\text{rel}}$	X	$k_{\text{rel}}$
Cl <sup>a</sup>	1.00	NO <sub>2</sub>	8.7	OPh	0.030	—S—C <sub>6</sub> H <sub>4</sub> - <i>p</i> -NO <sub>2</sub>	0.017
F	412	—OSO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	5.5	OCH <sub>2</sub> Ph	0.0011	—SO <sub>2</sub> Ph	0.0088
Br	1.17	—O—C <sub>6</sub> H <sub>4</sub> - <i>p</i> -NO <sub>2</sub>	2.9	OMe	0.0017	—S—Ph	0.0010
I	0.26	—OAc	0.06	—SO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub> - <i>p</i> -NO <sub>2</sub>	0.11	—CN	0.001

<sup>a</sup> The rate of chlorine displacement ( $k = 66 \times 10^{-6} \text{ l. sec}^{-1} \text{ mole}^{-1}$ ) is taken as a reference.



TABLE 28. Relative rates of displacement of halogens from halonitrobenzenes.

	Reagent and solvent	Temp. °C	Relative rate $k_I = 1.00$ , unless stated otherwise				Reactivity	Ref.
			Br	Cl	F			
1-X-2-NO <sub>2</sub>	MeO <sup>-</sup>	0	2.83	6.95	15350		I < Br < Cl << F	136
		50	2.13	3.03	2185		I < Br < Cl << F	136
		100	1.54	1.51	478		I < Br ~ Cl << F	136
	Pip. <sup>a</sup>	70	2.56	1.37	21.6			
		80	2.46	1.34	22.9		I < Cl < Br < F	85
		90	2.42	1.29	23.1			
	Pip.	45	2.95	1.43			I < Cl < Br	41
		75	2.54	1.11				
		50	2.06	2.77				
	MeO <sup>-</sup>	100	2.18	2.27				
1-X-4-NO <sub>2</sub>		0			865		I < Br < Cl << F	128, 132
					390		I < Br ~ Cl << F	128, 132
					2550		I << F	156
	EtO <sup>-</sup>	90.8	11.8	13.6	3100		I < Br < Cl << F	19
	MeS <sup>-</sup>	0			3720		I << F	156
	Pip.	90	3.48	2.70	26.3		I < Cl < Br < F	85
		75	4.00	1.45			I < Cl < Br	41
	Pip.	100	2.20	0.82			Cl < I < Br	41
		50	4.50	3.84	1585		I < Cl < Br << F	114
	DMSO				700		Cl << F	173
1-X-2,4-(NO <sub>2</sub> ) <sub>2</sub>	HO <sup>-</sup>	25		1.00			Br >> Cl >> F	327
	H <sub>2</sub> O				0.06			
	acetone	109	120	1.00			I < Br < Cl << F	128
	KI	50	2.60	4.16	5000		I << F	156
	MeO <sup>-</sup>	0			5780			
1-X-2,4-(NO <sub>2</sub> ) <sub>2</sub>		35	3.00	4.70	7130		I < Br < Cl << F	121

MeS <sup>-</sup> SO <sub>3</sub> <sup>-</sup>	MeOH 60% EtOH—H <sub>2</sub> O	0			372000	I	I < Cl < Br << F	156
		0	2.05	1.32	106	I	I < Cl < Br << F	29
		30	1.52	1.37	48.5	I	I < Cl < Br << F	29
		100	0.88	1.39	11.8	Br	Br < I < Cl < F	29
PhS <sup>-</sup>	MeOH	0	1.29	0.75	20.0	Cl	Cl < I < Br << F	70
NH <sub>3</sub>	MeOH	50				I	I < Br ~ Cl < F	292
n-BuNH <sub>2</sub>	CHCl <sub>3</sub>		3.2	2.3		I	I < Cl < Br	107
i-BuNH <sub>2</sub>	DMF		6.95	10.0		I	I < Br < Cl	107
Pip.	MeOH	0	4.31	4.27	3280	I	I < Br ~ Cl << F	67, 69
Pip.	benzene	25		1	7		Cl < F	94
2-Me-pip.	benzene	25		1	35		Cl << F	94
2,6-(Me) <sub>2</sub> -pip.	benzene	25		1	25		Cl << F	94
PhNH <sub>2</sub>	EtOH	50	3.27	2.18	128	I	I < Cl < Br << F	79
PhNH <sub>2</sub>	EtOH		1.51	1.00	62.5	Cl	Cl < Br << F	79, 294
PhNH <sub>2</sub>	EtOH	50	3.21	2.06	128	I	I < Cl < Br << F	295
PhNH <sub>2</sub>	acetone	50		1.75	22.0		Cl < F	30
PhNHMe	PhNO <sub>2</sub>	120	46.4	15.1	1.00	Br	Br > Cl > F	294
PhNHMe	EtOH	50	3.02	1.37	1.00	Br	Br > Cl > F	294
PhNHMe	EtOH	67.2	2.78	1.00	1.00	Br	Br > Cl = F	72
PhNHMe	EtOH + 0.1 M							
	K-acetate		2.55	1.00	12.1	Cl	Cl < Br < F	72
Pyridine	acetone	50		6.54	21.3		Cl < F	30
1-X-2,6-(NO <sub>2</sub> ) <sub>2</sub>	EtOH	50	4.40	2.38	105	I	I < Cl < Br << F	279
1-X-2,4-(NO <sub>2</sub> ) <sub>2</sub>	acetone	109	125	1.00	0.12	Br	Br >> Cl > F	327
1-X-2,4,6-(NO <sub>2</sub> ) <sub>3</sub>	H <sub>2</sub> O	25		1	22000		Cl << F	175
	H <sub>2</sub> O	25		1	1385		Cl << F	175
OH <sup>-</sup>	EtOH	50	5.10	3.55	355	I	I < Cl < Br << F	295
PhNH <sub>2</sub>								

<sup>a</sup> Pip. = piperidine.

negative inductive effect of fluorine<sup>382</sup> which facilitates C—N bond making more than with other halides, while C-halogen bond rupture is not a rate limiting factor (contrary to aliphatic  $S_N2$  displacements<sup>396</sup>). This is a logical explanation, but other factors<sup>132</sup> may also partly contribute to the high reactivity of fluorine such as hydrogen bonding with amines<sup>30,79</sup>, solvation energy of the transition state<sup>79,98,121</sup> and steric factors<sup>132,156</sup>.

Table 28 gives a further illustration on the dependence of halogen reactivity on substrate, nucleophile, solvent, and temperature. It is particularly illustrative to notice that in the reaction of *iodide ion* with 2,4-dinitrohalobenzenes the fluorine isomer is least reactive contrary to the reaction with most other nucleophiles. The weak C—I bond in the intermediate Meisenheimer complex makes the return reaction to starting material important ( $k_{-1}$  relatively large) and thus C—F rupture becomes a rate limiting factor (cf. the kinetic expression in section III.2). Since of all the C-Hal. bonds, the C—F bond is strongest, displacement of fluorine is slowest. In those reactions where the second step is in part rate limiting, solvent changes affect fluorine displacement much more strongly than other halogen displacements because small ions gain more energy by solvation than large ones<sup>24</sup>.

As a rule of thumb, Miller and Wong<sup>156</sup> state that in protic solvents halogen displacement will increase from I to F with first row nucleophiles and with very strong nucleophiles ( $\text{CH}_3\text{S}^-$ ). Nucleophiles derived from heavy elements show the reverse order, because bond-breaking becomes rate limiting.

Table 29 shows that the relative reactivity of fluorine increases on increasing nitro activation, in accordance with calculated  $\pi$ -electron densities<sup>175</sup>.

TABLE 29. Replacement rate of several substituted polynitrobenzenes in reaction with aniline in ethanol at 50°<sup>295</sup>.

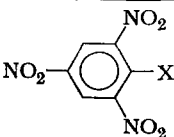
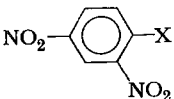
	X:	I	F	Cl	Br	NO <sub>2</sub>
	k:	0.94	334	4.79	3.34	4210
	10 <sup>4</sup> · k:	1.31	168	4.20	2.70	2110

TABLE 30. Relative reactivities for various nucleophiles.

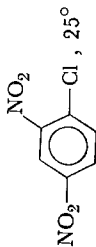
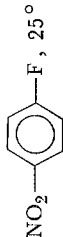
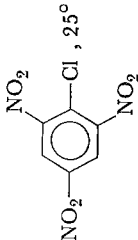

$k_{\text{relative}}$			
	 $\text{NO}_2$ -Cl, $25^\circ$	 $\text{NO}_2$ -F, $25^\circ$	 $\text{NO}_2$ -Cl, $25^\circ$
	60% dioxan- $\text{H}_2\text{O}^{55,71}$	$\text{MeOH}^{23}$	$\text{MeOH}^{23}$
$\text{MeOH}$		$\sim 10^{-9}$	$1.1 \times 10^{-9}$
$\text{Cl}^-$		$\sim 10^{-6}$	$1.1 \times 10^{-6}$
<i>m</i> -nitroaniline		$3 \times 10^{-4}$	$3.3 \times 10^{-2}$
aniline		1.00	1.00
$\text{OH}^-$	0.0725		
$\text{N}_2\text{H}_4$	1.00		
$\text{PhO}^-$	3.51		
$\text{MeO}^-$	10.8		
piperidine	33		
$\text{PhS}^-$	67.7	60	
	20000	10700 <sup>70</sup>	
		10100 <sup>70</sup>	

TABLE 31. Relative rates of some nucleophilic reactions.

X	Positions of NO <sub>2</sub> groups			Ref.
		Solvent	Sequence of nucleophilic reactivity of Y <sup>⊖</sup>	
NO <sub>2</sub>	2,4	Dioxan, MeOH or DMF	NHMe <sub>2</sub> > MeS <sup>-</sup> > MeO <sup>-</sup> > SO <sub>3</sub> <sup>=</sup> > MeSO <sub>2</sub> <sup>-</sup>	249
F	2,4	ROH <sup>a</sup>	<i>i</i> -PrO <sup>-</sup> > EtO <sup>-</sup> > MeO <sup>-</sup> 19.7      8.48      1.89	166
F	4	DMSO	MeO <sup>-</sup> ~ PhCH <sub>2</sub> O <sup>-</sup> > PhO <sup>-</sup> > <i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> O <sup>-</sup>	114
Br	2,4	MeOH	PhS <sup>-</sup> > <i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> O <sup>-</sup> > MeO <sup>-</sup> > PhNH <sub>2</sub> > > <i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> <sup>-</sup> > SCN <sup>-</sup> > I <sup>-</sup>	98
I	2	MeOH	MeO <sup>-</sup> > N <sub>3</sub> <sup>-</sup> > PhO <sup>-</sup> > SCN <sup>-</sup> 1.00      0.056      0.037      0.0017	145

<sup>a</sup> R = alkyl.

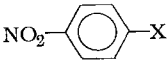
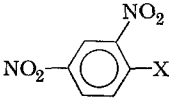
## 8. Reactivity of nucleophiles

The relative reactivities of some common nucleophiles in aromatic halogen displacement are listed in Table 30. The data show that the weakly basic thiophenolate anion is highly reactive like in aliphatic  $S_N2$  substitution. Apparently polarisability and not only basicity is important in both nucleophilic aromatic and aliphatic substitutions. The same is true for sulphite ion<sup>29</sup>. The high reactivity of alkoxides in comparison with hydroxides makes alcoholic solvents for alkali hydroxides unsuitable if ether formation is to be avoided in the preparation of phenols<sup>52,162-166,174,176,181,397</sup>. Not only hydroxide ions, but also much weaker bases such as amines produce in alcoholic solution reactive alkoxy ions (equation 27). Despite their low equilibrium concentration<sup>118</sup> these can lead to very high yields of ethers (up to 97%)



The nucleophilicity of alkoxides and phenoxides (Table 31) increases with basicity as long as steric factors do not dominate<sup>166</sup>. For many reactions ethoxide ion is found to be 3-8 times more reactive than methoxide<sup>286</sup>. Table 31 furthermore shows the reactivity of alkoxides in relation to some other nucleophiles. Relative reactivities of nucleophiles (e.g.  $PhS^-$  and  $MeO^-$ ) depend strongly on the nature of the substrate, as seen in Table 32 (cf. also Table 26). Bunnett<sup>67,73,74</sup> has furthermore concluded that in general a highly polarizable nucleophile ( $PhS^-$ ) displaces the most polarizable

TABLE 32. Relative reactivities of thiophenoxide and piperidine *vs* methoxide, illustrating the influence of a polarisability factor<sup>70</sup>.

					
X	$k_{PhS^-}/k_{MeO^-}$	X	$k_{PhS^-}/k_{MeO^-}$	$k_{pip.}^a/k_{MeO^-}$	
F	1.00	F	59	0.85	
Cl	38	Cl	1950	0.98	
		Br	4850	1.43	
		I	16800	1.48	

<sup>a</sup> pip = piperidine.

halogen (I) with greater ease. This has led to the view that London forces are operating in reaching the transition state<sup>29,49,73,74</sup>.

Theoretical calculations by Miller<sup>153,156</sup> and by Hill<sup>159</sup> in which such factors are neglected nevertheless show good agreement with experimental values for such reactions as collected in Table 33. The real

TABLE 33. Relative reactivities of various nucleophiles in reaction with some fluoro- and iodonitrobenzenes.

Substrate	Reagent in MeOH, 0°			
	N <sub>3</sub> <sup>-</sup>	MeO <sup>-</sup>	MeS <sup>-</sup>	PhS <sup>-</sup>
1-F-4-NO <sub>2</sub>	1.00	4.05 × 10 <sup>3</sup>	83.2 × 10 <sup>3</sup>	5.02 × 10 <sup>3</sup>
1-I-4-NO <sub>2</sub>	2.37 × 10 <sup>-3</sup>	1.58	22.4	2.19 × 10 <sup>3</sup>
1-F-2,4-(NO <sub>2</sub> ) <sub>2</sub>	1.00	85.2	9.75 × 10 <sup>3</sup>	6.32 × 10 <sup>3</sup>
1-I-2,4-(NO <sub>2</sub> ) <sub>2</sub>	0.85 × 10 <sup>-3</sup>	15.1 × 10 <sup>-3</sup>	20.0 × 10 <sup>-3</sup>	254

importance of London forces remains therefore uncertain<sup>49,98,159,160</sup>. Although there is generally no parallel between basicity (proton affinity) and nucleophilicity (carbon basicity)<sup>97</sup> there is good correlation within closely related series of reagents<sup>81,82,283</sup>.

The Brönstedt relation

$$\log k = \alpha pK_a + \beta$$

correlates nucleophilicity with basicity and applies to a number of substituted anilines and phenoles<sup>9,90,113,167,173,175,398</sup>. The constant  $\alpha$  is a measure for the reactivity of the nitroaromatic substrate. Anilines follow the relationship better than alkoxy anions the latter being more reactive than predicted from their  $pK_a$  values<sup>9</sup>. The Hammett-relationship provides another way of expressing quantitatively the reactivity relationships of amines or phenoles.

The large negative  $\rho$ -values collected in Table 34 reflect the importance of a high electron density at nitrogen or oxygen in the attacking nucleophile<sup>307</sup>. The  $\rho$ -value has been taken as a measure for the progress of bond-making in the transition state<sup>323,346</sup>. However, this approach should be made with caution. For instance in the reaction with 2,4-dinitrochlorobenzene, benzylamines show similar reactivity as anilines, yet the  $\rho$ -values are vastly different ( $\rho = -0.77$  and  $-3$  to  $-4$ , respectively). The reason need not be sought in the various degrees of bond-making in the transition state, but rather in the fact that the methylene group in benzylamines acts as a poor conductor of substituent effects<sup>305</sup>.

TABLE 34. Substituent effects in nucleophilic reagents, as correlated by the Hammett equation ( $n$  is the number of reagents used,  $r$  is the correlation coefficient).

Substrate	Nucleophile	Solvent	Temp. °C	$n$	$\rho$	$r$	Ref.
1-F-2,4-(NO <sub>2</sub> ) <sub>2</sub>	anilines	EtOH	20	6	-4.243	0.998	79, 393, 404
			30	6	-4.106	0.998	79, 393, 404
			40	6	-4.006	0.998	79, 393, 404
1-Cl-2,4-(NO <sub>2</sub> ) <sub>2</sub>	anilines		25	5	-3.976	0.967	393, 404, 405
			35	10	-3.204	0.992	393, 404, 405
			45	10	-3.055	0.993	393, 404, 405
			100	10	-2.415	0.979	393, 404, 405
			25	10	-3.190	—	406
1-Cl-2,4-(NO <sub>2</sub> ) <sub>2</sub>	phenoxides	80% dioxan-H <sub>2</sub> O	65	7	-1.8	—	323
		MeOH	25.9	5	-2.16	—	303
		60% DMSO-MeOH	25.9	5	-1.88	—	303
		80% DMSO-MeOH	25.9	5	-1.80	—	303
1-Cl-2,4-(NO <sub>2</sub> ) <sub>2</sub>	benzylamines	EtOH	45	6	-0.786	0.997	305
				11	-0.762	0.996	305
1-Cl-2,4-(NO <sub>2</sub> ) <sub>2</sub>	benzoates	60% dioxan-H <sub>2</sub> O	93	3	-0.20	—	346
1,4-Cl <sub>2</sub> -2-NO <sub>2</sub>	phenoxides	80% dioxan-H <sub>2</sub> O	65	7	-1.8	—	323
1-Cl-2,4,6-(NO <sub>2</sub> ) <sub>3</sub>	anilines	benzene	25	5	-4.79	—	257
1-Cl-2,4-(NO <sub>2</sub> ) <sub>2</sub> -naphthalene	anilines		25	6	-3.728	0.987	393
6-Cl-3-NO <sub>2</sub> -pyridine	anilines	EtOH	65	5	-3.687	0.975	81, 393
2-Cl-3-CN-5-NO <sub>2</sub> -pyridine	anilines		20	4	-3.39	—	90
2-Cl-3-CN-5-NO <sub>2</sub> -6-Me-pyridine	anilines	MeOH	10	3	-3.24	—	90
2-Cl-3-CN-5-NO <sub>2</sub> -4,6-Me <sub>2</sub> -pyridine	anilines	MeOH	10	3	-3.32	—	90



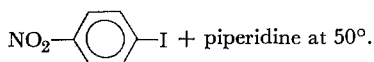
Further factors of importance in determining the nucleophilicity are steric effects<sup>116,117</sup>, hydrogen bonding<sup>30,79,294</sup> and nature of the solvent<sup>100,326</sup>.

Characterizing the nucleophilicity of a reagent in general poses a very complex problem<sup>9,10,399-403</sup>.

## 9. Medium effects

Because the reaction of amines with nitrohalobenzenes takes place via an intermediate with charge separation it is not surprising that rates increase with solvent polarity<sup>3,47</sup>. For the particular iodine displacement in Table 35 the rate in DMSO is more rapid than in

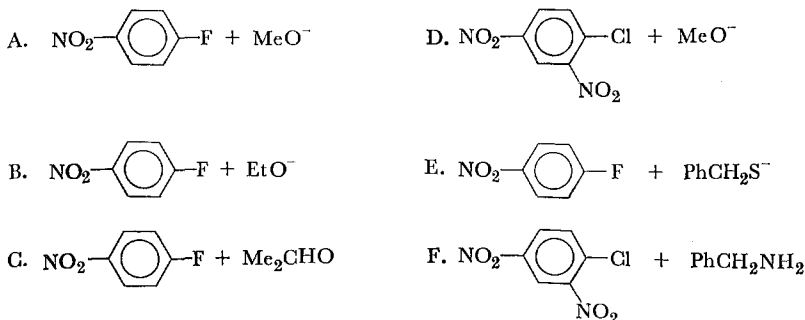
TABLE 35. The influence of solvents on the rate of the reaction<sup>115</sup>



	$10^6 \cdot k$
Dimethyl sulfoxide	18.4
Dimethylformamide	6.9
Acetonitrile	2.1
Benzonitrile	1.10
Methyl ethyl ketone	1.01
Ethyl acetate	0.40
Benzene	0.047
Ethanol	0.047

benzene or ethanol by a factor of nearly 400. Reactions in alcohols can be easily speeded up by addition of some DMSO and a four-fold rate increase with no more than 20% DMSO is no exception<sup>303</sup> (Table 36). Furthermore DMSO has the advantage that it tends to suppress side reactions<sup>118</sup> which makes it particularly suitable for kinetic measurements<sup>116</sup>.

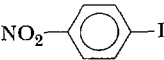
In many cases the response to change in solvent polarity is largest for the strongest nucleophile. In one particular iodine displacement (Table 37) a solvent change from methanol to DMF gives acceleration factors in the order of 10 and 100,000<sup>100</sup> for phenoxide and thiophenoxide ion, respectively. Certain displacements which are impossible or difficult in protic solvents, can sometimes be effected in aprotic DMSO,<sup>150,169,407</sup> e.g. chlorine displacement by fluoride ion<sup>326</sup>. This

TABLE 36. Reaction rates in methanol-dimethyl sulfoxide mixtures at 25°<sup>303</sup>.

Vol. % DMSO	A	B	C	D	E	F
0	1.00	1.00	1.00	1.00	1.00	1.00
20	4.29	3.36	11.9	4.87	5.72	2.71
40	23.7	21.3	77.8	21.6	35.7	
60	171	119	380		266	
80	2120	908				
90						72.9

can be explained by the fact that the nucleophilicity of anions increases in aprotic dipolar solvents because of decreased solvation<sup>303</sup>; (cf. also reference 101, 168, 177). It was pointed out earlier (section II.2), that hydrogen bonding is important in many aminodehalogenations<sup>50,110</sup>. It should therefore not be too surprising that *o*- and *p*-chloronitrobenzene show in their reaction with piperidine completely different solvent effects. For instance a change from benzene to methanol *decreases* the rate of displacement in the *ortho*-compound by a factor of 4, but in the *para*-compound it increases by a factor of 6<sup>46</sup>. Some general rules concerning the solvent action on

TABLE 37. Rate of deiodination of *p*-iodonitrobenzene by phenoxide and thiophenoxide at 0° in ethanol and dimethylformamide<sup>100</sup>.

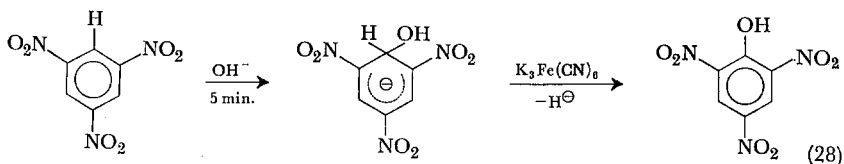
		MeOH	DMF
		$k_2 \times 10^4$	
 +	PhS <sup>-</sup>	0.034	820
	PhO <sup>-</sup>	0.004	0.066

aromatic nucleophilic substitution are given by J. Miller<sup>153</sup>. Solvent effects have been studied widely but nevertheless, many aspects remain too complex for unambiguous interpretation, and have mainly empirical value<sup>9,10,58,60,68,101,115,129,143,162,164-166,288,304,318,322,348,408</sup>.

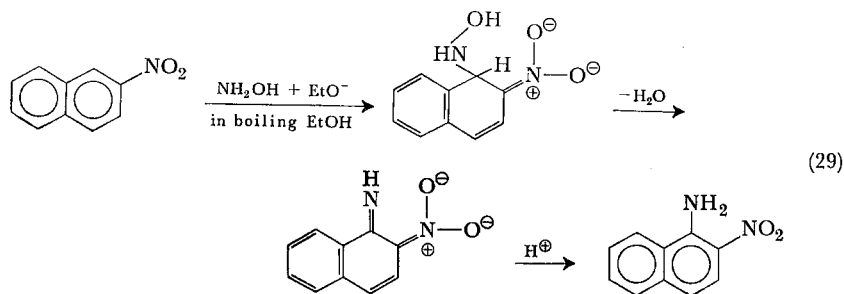
#### IV. NUCLEOPHILIC DISPLACEMENT OF OTHER GROUPS

##### I. Displacement of hydrogen

It was pointed out in the introduction that nitrobenzene is converted to *o*-nitrophenol upon heating with super-dry potassium hydroxide<sup>409</sup> especially in the presence of a weak oxidizing agent (equation 28),



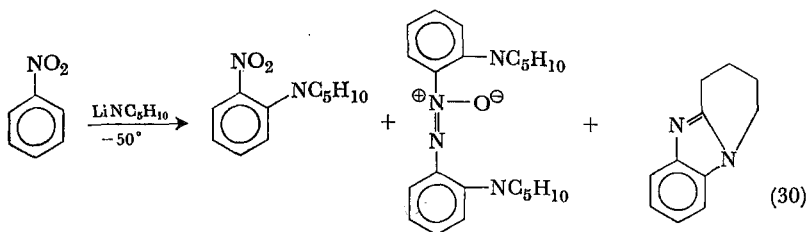
The interference of hydride ions is avoided in certain nucleophilic reactions of hydroxylamine. For instance with 2-nitronaphthalene a normal Meisenheimer complex<sup>410,411</sup> is formed but instead of losing hydride ion, water is eliminated in a facile 1,2-elimination process (equation 29),



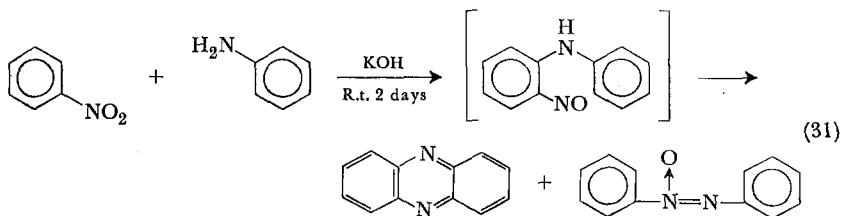
The high yield of 1-amino-2-nitronaphthalene shows that reduction of nitro groups is largely suppressed.

Metal salts of secondary amines are also good nucleophiles for displacement of hydrogen in aromatic nitro compounds. It depends somewhat mysteriously on reaction conditions as to which hydrogen is removed. In nitrobenzene *para*-hydrogen is displaced by sodium

piperidide in piperidine at room temperature<sup>412,413</sup>, whereas *ortho* hydrogen is displaced by lithium piperidide in ether at  $-50^\circ$ .<sup>414</sup> Reductive side reactions and condensations limit the practical usefulness of such reactions (equation 30).

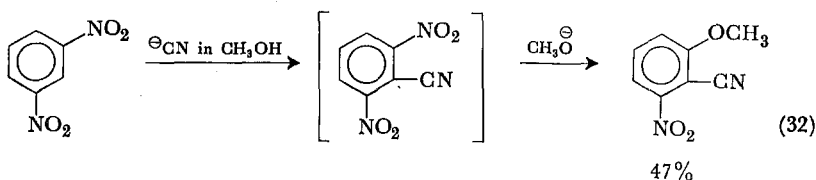


The tendency to form polycyclic products is also found in the reaction between nitrobenzene and aniline in the presence of sodium hydroxide<sup>415</sup> (equation 31).



The intermediate nitroso stage is supported by the isolation of some *p*-nitrosodiphenylamine.

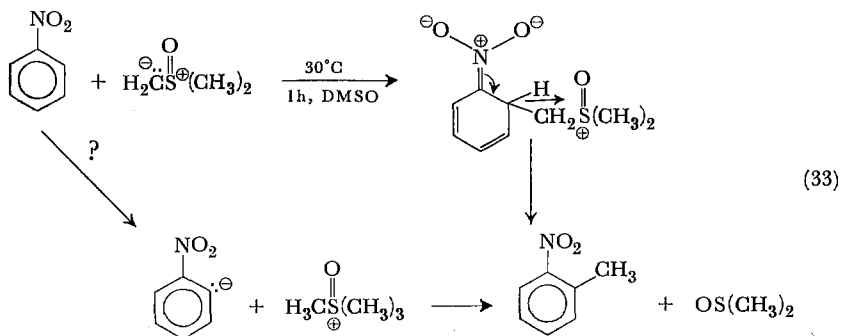
Hydrogen can also be displaced by the much weaker nucleophilic cyanide ion. With *m*-dinitrobenzene the *ortho* position with respect to both nitro groups is preferentially attacked by potassium cyanide in methanol<sup>416</sup>. The expected 2,6-dinitrobenzonitrile is not isolated as such, because one of the nitro groups is lost as nitrite ion either by attack of the solvent or by methoxy ions, which arise in small concentration from the equilibrium between cyanide ion and solvent (equation 32).



Similar examples of nucleophilic displacement of nitro groups under the influence of activating substituents (e.g. cyano and nitro groups) are given in the next section.

Other nucleophilic hydrogen displacements scattered in the older literature have been reviewed<sup>1</sup>.

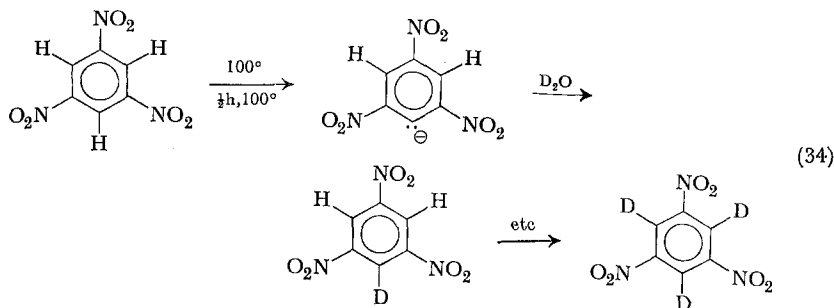
A remarkable application of nucleophilic hydrogen displacement is the introduction of methyl groups by dimethyloxosulfonium ylide. The latter is obtained from DMSO and methyl iodide *via* elimination of hydrogen iodide from the trimethyloxosulfonium salt by a suitable base<sup>417, 418</sup> (equation 33).



This vigorous reaction leads to a mixture of *o*- and *p*-nitrotoluene (ratio 2:3) in a total yield of 35 %. Without the activating influence of the nitro group the reaction is much slower. Triphenylphosphonium methyllide ( $\phi_3\text{P}=\text{CH}_2$ ) reacts similarly but yields are lower (up to 13 %). Other nitro compounds such as 1-nitronaphthalene, nitrotoluenes, nitroanisoles and chloronitrobenzenes are methylated in yields up to 25 %. Interestingly, in the three isomeric chloronitrobenzenes, hydrogen (in ortho position to the nitro groups) and not halogen is displaced.

A 'normal' nucleophilic displacement by an addition-elimination mechanism seems to explain the results adequately. However, in the highly polar solvent DMSO the 'carbon basicity' of the nucleophile may be decreased in favour of its 'hydrogen basicity'. In our opinion—as opposed to Traynelis and McSweeney—initial proton abstraction (arrow with question mark) can therefore not be ruled out *a priori*. This view is supported by the recent finding of almost complete replacement of the hydrogens in *s*-trinitrobenzene by deuterium<sup>419</sup> in a mixture of 90 % DMF-10 % deuterium oxide containing 0.01 M sodium deuteriooxide (equation 34). The choice of solvent is extremely important since in several other alkaline

media e.g. 8 M sodium hydroxide or pyridine no deuterium incorporation can be achieved<sup>420</sup>. In such media the nucleophile exerts its 'carbon basicity'<sup>97,101,421</sup> with predominant formation of Meisenheimer complexes. In DMF the nucleophile is strongly solvated and this somehow increases its 'hydrogen basicity'<sup>422</sup> and its capacity for proton abstraction from carbon. In *m*-dinitrobenzene



the proton 'between' the two nitro groups can similarly be exchanged<sup>206,208,423</sup> for tritium. By spectroscopic and tracer measurements Gold has definitely shown that a Meisenheimer complex—even if the majority of *m*-dinitrobenzene is present as a complex cannot be responsible for hydrogen exchange. The exchange takes place by proton abstraction from the small fraction of nitro compound present as such in the alkaline medium

A specific case of hydrogen replacement is found for *m*-nitrobenzal chloride<sup>424,425</sup> with  $X^-$  = Piperidine,  $\text{MeO}^-$  or  $\text{EtO}^-$  (equation 35).

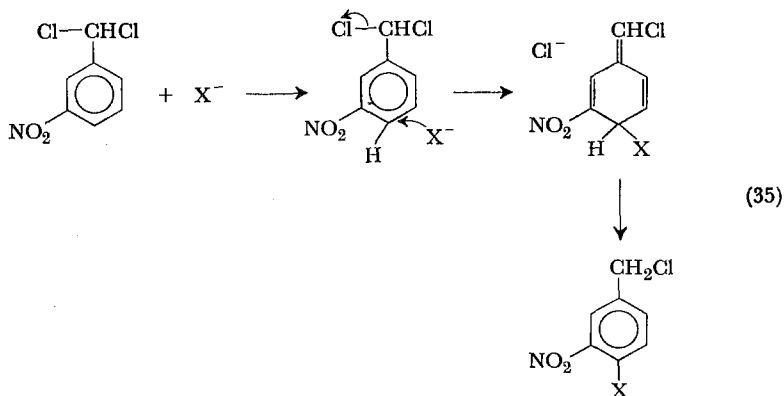


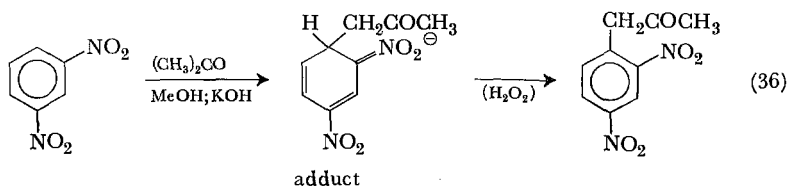
TABLE 38. Displacement of hydrogen in nitroaromatics.

Position of NO <sub>2</sub> group(s)	Subst.	Reagent	Solvent	Ref.
1		<i>t</i> -BuO <sup>-</sup>	<i>t</i> -BuOH—DMSO	427
		ND <sub>3</sub> liq.		428
1	3-R <sup>a</sup>	MeSO—CH <sub>2</sub> <sup>⊖</sup>	DMSO	418
1	4-R <sup>a</sup>	MeSO—CH <sub>2</sub> <sup>⊖</sup>	DMSO	418
1	3-CHCl <sub>2</sub> -4-OTs	piperidine	piperidine	424
		MeO <sup>-</sup> and EtO <sup>-</sup>	MeOH and EtOH	424, 425
1,3		D <sub>2</sub> O/NaOD	DMF	389, 419, 423
1,3		MeO <sup>-</sup> , T <sub>2</sub> O	MeOH, DMSO	208
		MeO <sup>-</sup>	DMSO	221
		OH <sup>-</sup>	several	247
		ND <sub>3</sub> liq.		428
1,4		ND <sub>3</sub> liq.		428
1,3,5		OH <sup>-</sup>	DMSO—H <sub>2</sub> O; D <sub>2</sub> O; DMF	206, 420, 419, 423
		MeO <sup>-</sup>	DMSO, MeOH	197, 204, 206, 208
		prim., sec., tert.-amines	several	207, 213, 215, 218, 309, 361, 362, 365
		EtO <sup>-</sup>	EtOH	214, 353, 362, 363, 429
		KCN	EtOH	212, 430
		OH <sup>-</sup>	H <sub>2</sub> O	314, 362, 370, 430-432
		SO <sub>3</sub> <sup>=</sup>		430
		SH <sup>-</sup>		430
		arom. amines		309, 361, 362, 364, 433
		piperidine		434
		NH <sub>3</sub> liq.		216
		<i>t</i> -BuOH		427
		OH <sup>-</sup>	H <sub>2</sub> O	195, 200, 201
		HNEt <sub>2</sub>	acetone	224
		MeO <sup>-</sup> , EtO <sup>-</sup>	several	221
		Na	ethylene glycol	222

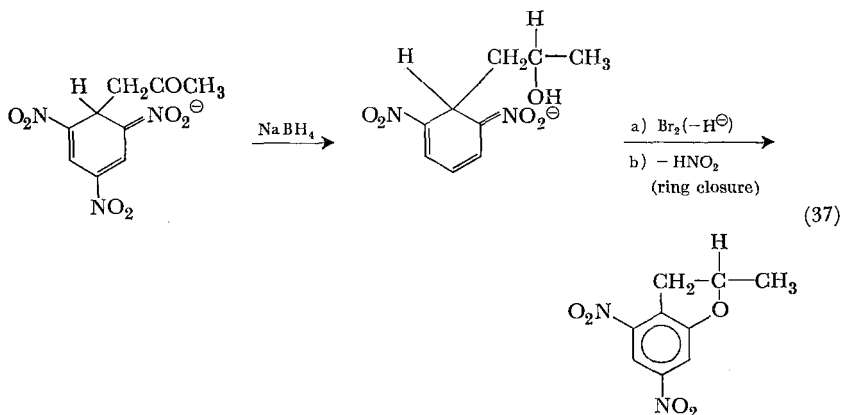
<sup>a</sup> R = alkyl.

A short discussion on these and other hydrogen replacements is given by Shatenstein<sup>426</sup>.

Table 38 gives a collection of some hydrogen displacements from nitro compounds. Carbanions derived from ketones (e.g. acetone) by removal of  $\alpha$ -hydrogen in alkaline media, can also displace hydrogen in aromatic nitro compounds but an oxidizing agent is necessary to remove hydrogen from the relatively stable adduct (the nitro compound itself is apparently not effective in this respect) (equation 36).



Because of the relative stability of the adducts and their characteristic colors, this reaction has found some use as a qualitative test for aromatic nitro compounds. When carried out with aqueous acetone in the presence of hydroxides it is known as the Yanowski reaction, with alcoholic acetone in the presence of alkoxides as the Zimmermann reaction. Evidence for the structure of the intermediate complex has been given by Severin and Schmitz<sup>435-437</sup> by reduction of the complex with  $\text{NaBH}_4$  (which does not attack the nitro group), followed by oxidation with bromine and isolation of a bicyclic ether (equation 37).



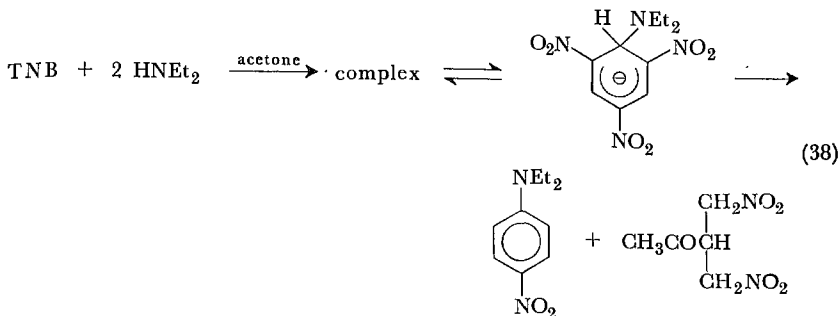
An extensive study of similar reactions was made by Pollitt and



Position NO <sub>2</sub>	Subst.	Reagent	Ref.
1		NaOH, acetone	368
	3-R <sup>a</sup>	OH <sup>-</sup> , acetone	438
	3-R <sub>1</sub> <sup>a</sup> -5-R <sub>2</sub> <sup>a</sup>	OH <sup>-</sup> , acetone	438
		OH <sup>-</sup> , acetone	368
		Na, acetone in <i>o</i> -xylene	229
1,3		60 reagents with activated methylene groups	439
		OH <sup>-</sup> , acetone	245, 250, 368, 440
		OH <sup>-</sup> , acetophenone	217, 440
		OH <sup>-</sup> , acetophenone in EtOH	441
		OH <sup>-</sup> , ketones	217
		EtO <sup>-</sup> , ketones	217
		Na, acetone in <i>o</i> -xylene	229
1,4		Na, acetone in <i>o</i> -xylene	229
	2,3-Me <sub>2</sub>	Na, acetone in <i>o</i> -xylene	229
2,4	1-OH	EtO <sup>-</sup> , acetone	437
		OH <sup>-</sup> , acetone	217, 235, 251, 368, 369
	1-R	OH <sup>-</sup> , acetone	250, 389
	1,5-Me <sub>2</sub>	OH <sup>-</sup> , acetone	235
	1,3-Me <sub>2</sub>	OH <sup>-</sup> , acetone	235
	1-Me-5-R	OH <sup>-</sup> , acetone	236
	1-OR	OH <sup>-</sup> , acetone	236
	1-Me-5,6-(OEt) <sub>2</sub>	OH <sup>-</sup> , acetone	235
	3,6-Me <sub>2</sub>	OH <sup>-</sup> , acetone	235
	1,3,5-Me <sub>3</sub>	OH <sup>-</sup> , acetone Na, acetone	229, 235
	1-Me	OH <sup>-</sup> , acetone	235
	3-Me	OH <sup>-</sup> , acetone	235
	1-R <sub>1</sub> -5-R <sub>2</sub>	OH <sup>-</sup> , acetone	389
3,5	1-R	OH <sup>-</sup> , acetone	236, 442-444
	1-R	OH <sup>-</sup> , acetophenones	443, 444
	1-SO <sub>3</sub> Ar	Na, ketones and esters	445
2,6	1-R	OH <sup>-</sup> , acetone	389
1,2,4		OH <sup>-</sup> , acetone	236
1,2,3	5,6-Me <sub>2</sub>	OH <sup>-</sup> , acetone	236
2,4,6	1-Me	OH <sup>-</sup> , acetone	235, 315, 316
	1-NMeNO <sub>2</sub>	OH <sup>-</sup> , acetone	315, 316
	1,3-Me <sub>2</sub>	Na, acetone in xylene	229, 235
	1-OH	OH <sup>-</sup> , acetone	313, 446
	1-OR	OH <sup>-</sup> , acetone	313
	1-R	OH <sup>-</sup> , acetone	313
	1-NR <sub>1</sub> R <sub>2</sub>	OH <sup>-</sup> , acetone	313
1,3,5		OH <sup>-</sup> and Na in acetone	229, 252, 235, 245, 315, 368, 440, 442, 447, 448
		OH <sup>-</sup> , acetophenone	440, 447, 448
		NHEt <sub>3</sub> , acetone	224, 363
		⊖CH <sub>2</sub> -CO-CH <sub>3</sub> , several solvents	221
		acetone	362
		EtO <sup>-</sup> , several ketones	435, 436
		NEt <sub>3</sub> , several ketones	223, 225

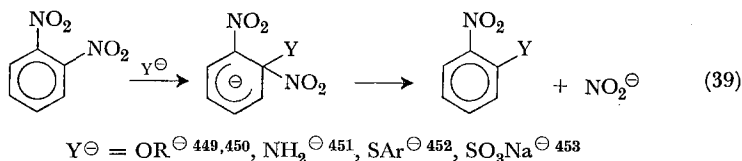
<sup>a</sup> R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> = alkyl.

Saunders<sup>389</sup>. Table 39 shows a number of these reactions which are often limited to a discussion of spectra. Very complicated reactions arise when acetone reacts with trinitrobenzene (TNB) in the presence of diethylamine. Among the products are aliphatic nitro compounds resulting from an intricate opening of the aromatic ring<sup>224, 225</sup> (equation 38),



## 2. Displacement of nitro groups

All nucleophilic displacements discussed so far take place under the activating influence of the nitro group. However, when activated by suitable electron withdrawing substituents, the nitro group itself may also be displaced<sup>114, 162, 181</sup>. Illustrative examples are found in the reaction of *o*- and *p*-dinitrobenzene with various nucleophiles, (Table 40) (equation 39),

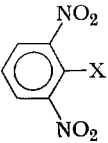
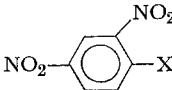
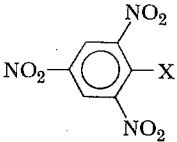


With hydroxide and alkoxide ions the nitro group is more easily displaced than chlorine from similarly activated positions<sup>1</sup>. Nevertheless reaction is slow at room temperature and is mostly carried out at elevated temperatures.

The rates of reaction in relation to the Hammett H-acidity function of the isomeric dinitrobenzenes with methoxide in methanol have been studied by Schaal and coworkers<sup>454, 455</sup>.

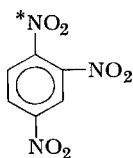
*m*-Dinitrobenzene does not eliminate nitro groups and this property has been used in the past to remove *o*- and *p*-dinitrobenzene as the corresponding nitrophenolates from crude *m*-dinitrobenzene

TABLE 40. Rates of reaction of several polynitrobenzene derivatives with aniline in EtOH at 50° 279.

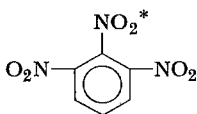
$10^4 \cdot k_2 \text{ l. mole}^{-1} \cdot \text{sec}^{-1}$			
X			
NO <sub>2</sub>	3260	2110	42100
F	87.7	168	3340
Cl	1.98	2.69	33.4
Br	3.66	4.05	47.9
I	0.832	1.31	9.40

by heating at 80° with 1% sodium hydroxide<sup>456</sup>. With stronger alkali and at higher temperatures *m*-dinitrobenzene does react also and is partly reduced to an azoxy derivative, by reactions involving not nitro but hydrogen displacement as described in the previous section. Presumably this reaction also occurs to some extent with dilute sodium hydroxide and this may partly explain why the purification with alkali is not perfect. A better method is treatment of crude *m*-dinitrobenzene with sodium sulphite, which removes the *ortho*- and *para*-isomers by conversion into soluble nitrosulphonates<sup>457</sup>. Other aromatic compounds with a mobile nitro group<sup>458,459</sup> are involved in the reaction of cyanide ion in methanol with *m*-dinitrobenzene<sup>456</sup> (equation 32).

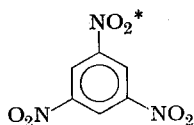
Numerous reactions are recorded with tri-, tetra- and more highly substituted aromatics. In all three isomeric trinitrobenzenes **2**, **3** and **4** one nitro group—indicated by an asterisk—can be displaced by an alkoxy<sup>247,460</sup> or amino<sup>295,461</sup> group.



(2)



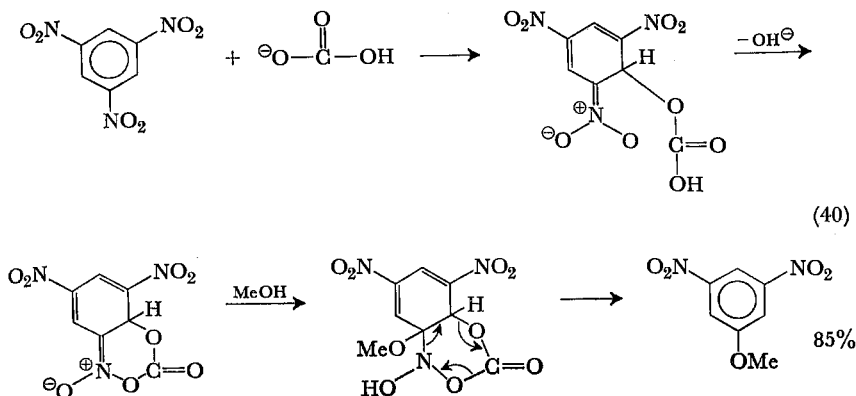
(3)



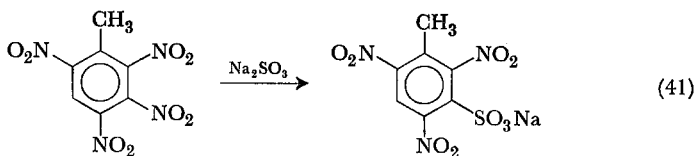
(4)

3,5-Dinitroanisole is conveniently prepared from 1,3,5-trinitrobenzene by boiling with sodium methylate<sup>462</sup>.

More recently potassium bicarbonate has been recommended as a specific catalyst in methanol effecting the exchange of a nitro group for a methoxy group. Interestingly other weak bases like sodium acetate are far less effective. The following mechanism, which bears some analogy with the von Richter reaction (cf. section VII.2) has been suggested<sup>463</sup> as a logical pathway (equation 40).



Many sterically hindered nitro groups are displaced very smoothly even at low temperatures<sup>466</sup> and this is used to advantage in the explosives industry for the technical purification of 2,4,6-trinitrotoluene with sodium sulphite, which removes preferentially unsymmetrical polynitro compounds<sup>465</sup> as soluble sulphonates (equation 41).



Overcrowding of nitro groups increases their mobility enormously as shown by the moisture sensitivity of 1,2,3,5-tetranitrobenzene<sup>466</sup> which decomposes into picric acid, and of hexanitrobenzene<sup>467</sup> which gives trinitrophenol. Such reactions have more theoretical than practical significance. An interesting case arises when competitive displacement of halogen and nitro groups from one molecule is possible. When flanked by two ortho-chlorine atoms the nitro group can not fully exert its  $-M$  effect because of steric

TABLE 41. Nucleophilic displacement of nitro groups from nitroaromatic systems.

Position of NO <sub>2</sub> group	Substituents	Reagent	Solvent	Ref.
1	3-CH(OMe) <sub>2</sub> -4-OTs	MeO <sup>-</sup>	MeOH	424
	2-R <sub>1</sub> <sup>a</sup> -5-R <sub>2</sub> <sup>a</sup>	quinoline	quinoline	470
	4-R <sup>a</sup>	MeO <sup>-</sup>	MeOH	122, 139
	3,5-(CF <sub>3</sub> ) <sub>2</sub>	MeO <sup>-</sup>	MeOH, DMF, pyridine	247
1,2		OH <sup>-</sup> and OR <sup>-a</sup>	PhH	162, 181
		MeO <sup>-</sup>	H <sub>2</sub> O and H <sub>2</sub> O—ROH <sup>a</sup>	455
		H <sub>2</sub> NNH <sub>2</sub>	MeOH	310
1,3		MeO <sup>-</sup>		247
1,4	4,5-Br <sub>2</sub>		benzene, MeOH,	
	5-CF <sub>3</sub>		DMF, pyridine	
2,4		OH <sup>-</sup> and OR <sup>-</sup>	H <sub>2</sub> O and H <sub>2</sub> O—ROH	162, 181
		MeO <sup>-</sup>	MeOH	454
3,4	1-SO <sub>2</sub> -R	piperidine	DMSO	114
2,6	1-Cl	MeO <sup>-</sup>	MeOH	345
	1-SO <sub>2</sub> -R	Ar <sub>1</sub> -SO <sub>2</sub> -S-Ar <sub>2</sub>		340
1,2,4		piperidine; Me <sub>2</sub> NH; EtNH <sub>2</sub>	dioxan	345
	1-SO <sub>2</sub> -R	MeO <sup>-</sup>		
1,2,3		SO <sub>2</sub> Me <sup>-</sup>	MeOH	345
			dioxan, DMF,	249
1,3,5	5-Me	H <sub>2</sub> NOH	MeOH	469
		aniline, piperidine	EtOH	67, 279
1,2,4,6		PhS <sup>-</sup>	EtOH, MeOH	70
		HCO <sub>3</sub> <sup>-</sup>	MeOH	463
		H <sub>2</sub> O, OH <sup>-</sup>	aq. MeOH	171, 175
		aniline	H <sub>2</sub> O	295
		HCl; HBr; POCl <sub>3</sub> + pyridine	EtOH	471-473
		HCl; HI; POCl <sub>3</sub> + pyridine		471
	3-OH	HCl + dimethylaniline;		471
	3-NH <sub>2</sub>	POCl <sub>3</sub> + pyridine		
	5-OH	HCl; HI; POCl <sub>3</sub> ;		473
		POCl <sub>3</sub> + pyridine		
	5-NH <sub>2</sub>	HCl		473
		NH <sub>3</sub> liq		216

<sup>a</sup> R, R<sub>1</sub>, and R<sub>2</sub> = alkyl.

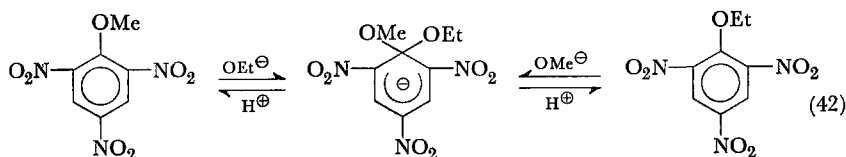
hindrance. Thus the mobility of chlorine is diminished and displacement of nitro groups becomes competitive. In pentachloronitrobenzene the nitro group is even displaced in preference to any chlorine<sup>468</sup>.

Other electron-withdrawing substituents which promote the mobility of an ortho-nitro group are the diazonium group<sup>411</sup> and the sulfonyl group<sup>460</sup>. Many other examples of nitro group displacement in the older literature have been collected by Bunnett and Zahler<sup>1</sup>. Because compounds with mobile nitro groups are less easily available than those with mobile chlorine, they have received less attention and most of the work—including recent investigations<sup>469</sup>—has been confined to product analysis rather than kinetics.

Recent examples of the mobility<sup>171,295,326</sup> of the nitro group in activated aromatic systems are collected in Table 41.

### 3. Displacement of alkoxy- and aryloxy groups in hydrolysis and trans-etherification

Displacement of an alkoxy or aryloxy group from nitro-activated aromatic ethers is usually more difficult than displacement of halogen. This is best understood in terms of leaving group stability. Other things being equal, halogen is removed as anion more easily from a Meisenheimer complex than an alkoxy ion. One of the first studies in this field was connected with picryl ethers (equation 42).



When 2,4,6-trinitroanisole reacts with ethylate ion the intermediate complex can be isolated<sup>474</sup>. Through the presence of three nitro groups it is so stable that neither of the alkoxy groups is lost in alkaline medium at room temperature. However, upon heating (or treatment with water<sup>230</sup>) one alkoxy group can be split off, leaving either the original trinitroanisole or the phenethole. Because the methyl group has a slightly smaller +I effect than the ethyl group, methoxy is a better leaving group than ethoxy.

Recently these decompositions have also been studied by Murto

TABLE 42. Hydrolysis and transesterification of alkoxy- and aryloxy-nitro-aromatic compounds.

Position of NO <sub>2</sub> group	Alkoxy- and aryloxy groups	Substituents	Reagent	Solvent	Ref.
1	4-MeO		MeO <sup>-</sup>	MeOH	153, 372
	2-OMe	5-R <sup>a</sup>	ROH <sup>a</sup> + KOH	ROH	237, 242
	4-OMe	3-R	ROH + KOH	ROH	237
	1-OH		MeO <sup>-</sup>	MeOH—DMSO	206, 209
	1-OMe		NaOH	H <sub>2</sub> O	484, 485
	1-OMe		KOH + Et <sup>18</sup> OH		239
	1-OMe		MeO <sup>-</sup>	MeOH—DMSO	206, 209, 221, 226
	1-MeO		MeO <sup>-</sup>	MeOH	372, 374, 485
	1-OMe		RO <sup>-</sup>	ROH, benzene	231, 242, 244
	1-OMe		MeO <sup>-</sup> , T <sub>2</sub> O	MeOH	153, 108
2,4	1-O <sup>1</sup> CH <sub>3</sub>		MeO <sup>-</sup>	MeOH	475
	3-OMe		MeO <sup>-</sup>	benzene	244
	1,5-(OMe) <sub>2</sub>		MeO <sup>-</sup> ; KOH + ROH	DMSO; dioxan	226, 348
	1-OR		OH <sup>-</sup>	H <sub>2</sub> O and H <sub>2</sub> O—ROH	162, 164, 173
	1-OR		KOH + ROH	benzene	232, 233, 248
	1-OCH <sub>2</sub> CH <sub>2</sub> OH		intramolecular	MeOH; DMSO	226, 367
	1-OC <sub>6</sub> H <sub>4</sub> -R		MeO <sup>-</sup>	MeOH	130
	1-OAr		KOH + HOAr	DMF	253-255, 454
	1-OAr		NaOH	H <sub>2</sub> O	273
	1,6-(OMe) <sub>2</sub>		OH <sup>-</sup>	H <sub>2</sub> O	202
	3,6-(OH) <sub>2</sub>		OH <sup>-</sup>	H <sub>2</sub> O	202
	1-OMe	5-Me	KOH	MeOH	348
	1-OMe	6-R	MeO <sup>-</sup>	MeOH, DMF	367
	1-OEt		MeO <sup>-</sup>	DMSO	226
	1-OMe	4-R	MeO <sup>-</sup>	MeOH, DMF	367
	1-OMe		MeO <sup>-</sup>	DMSO	226
	1-OEt		MeO <sup>-</sup>	DMSO	226
2,6					

2,4,6	1-OCH <sub>2</sub> CH <sub>2</sub> OH	MeO <sup>-</sup>	DMSO	226
	1-OMe	H <sub>2</sub> O, MeOH		178
	1-OMe	OH <sup>-</sup> , ROH	H <sub>2</sub> O; ROH <sup>a</sup> , benzene	200, 230, 238
	1-OMe	MeO <sup>-</sup>	DMSO	226
	1-OMe	RO <sup>-</sup>	several	211, 214, 220, 221
	1-OMe	OH <sup>-</sup> , Me <sup>18</sup> OH		241
	1-O <sup>1</sup> CH <sub>3</sub>	MeO <sup>-</sup>	MeOH	475
	1-OEt	EtO <sup>-</sup>	several	180, 218, 221, 192
	1-O- <i>i</i> -Pr	<i>i</i> -PrO <sup>-</sup>	several	220
	1-OPh	OH <sup>-</sup> , H <sub>2</sub> O	H <sub>2</sub> O	175
	1-OPh	MeO <sup>-</sup>	MeOH	325
	1-OPh	NEt <sub>3</sub> acetone		226
	1-OR	RO <sup>-</sup>		178, 179
	1-OCH <sub>2</sub> CH <sub>2</sub> OH	intramolecular		221, 222
	1-OR	H <sub>2</sub> O, OH <sup>-</sup>	H <sub>2</sub> O	172, 175
	1-OAr	OH <sup>-</sup> ; H <sub>2</sub> O	H <sub>2</sub> O	175
	1-OAr	MeO <sup>-</sup>	MeOH	325
	1-OH	OH <sup>-</sup>	H <sub>2</sub> O; DMSO	202, 206, 314, 371
	1-OMe	MeO <sup>-</sup>	MeOH; DMSO	196, 199, 204, 206, 209
	1-O- <i>i</i> -Pr	OH <sup>-</sup> , ROH	MeOH—DMSO	206
	1-OEt	OH <sup>-</sup> , <i>n</i> -PrOH	ROH-benzene	238
	1-OEt	NEt <sub>3</sub> /acetone		230
	1-OMe	MeO <sup>-</sup>	MeOH—DMSO	226
	1-n-OBu	<i>n</i> -BuO <sup>-</sup>		153, 196, 199, 204, 206,
	1-OMe	MeO <sup>-</sup>	several	209, 375
	1-OR	MeO <sup>-</sup>	MeOH	221
	1-OR	EtO <sup>-</sup>		372, 373
				366
				366

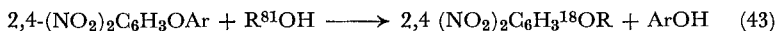
<sup>a</sup> R = alkyl.



and coworkers<sup>178-180</sup>. The ether oxygen in the Meisenheimer intermediate is protonated and a unimolecular decomposition follows. The same holds for other trans-etherifications with trinitroanisole and other nitro arylothers in reaction with alcohols as studied by Gitis<sup>229-249</sup> and Foster<sup>226</sup>. Although Meisenheimer complexes cannot always be isolated there seems little doubt that nucleophilic displacement of alkoxy groups from less activated nitro compounds proceeds similarly<sup>464</sup>, the only difference being a less deep saddle in the graphs of energy *vs* reaction-coordinate (cf. section III.1).

When *o*- and *p*-nitroanisoles are boiled with ethanol containing a small amount of potassium hydroxide the corresponding phenetoles are obtained in 70-90% yield<sup>476</sup>. The reactions are reversible with methanol in sealed tubes at 100°<sup>477</sup>, and this shows that the activation energy to form the Meisenheimer complex from mono-nitro aromatics is much higher than with more strongly activated aromatic ethers<sup>242</sup>. No such exchange could even be achieved with *p*-nitroanisole and isopropyl alcohol, isobutanol or phenol<sup>477</sup>.

Reactions of 2,4-dinitroanisole have been studied by Ogata and Okano<sup>477,478</sup> and by Gitis and Glaz<sup>231</sup> with various isomeric C<sub>3</sub>- and C<sub>4</sub>-alcohols (yield 73-77% after 10 h reflux). The rupture of the aryl-oxygen (not alkyl-oxygen) bond is demonstrated by a reaction of 2,4-dinitroanisole with <sup>18</sup>O-labeled ethanol, yielding the labeled phenetole<sup>239</sup> (equation 43),



With an activating methylsulfonyl group instead of one of the nitro groups trans-etherifications are equally smooth<sup>237</sup>. 2,4-Dinitrophenylbenzyl ethers react similarly with benzyl alcoholate<sup>248</sup>.

2,4-Dinitrophenyl *aryl* ethers are easily transesterified with aliphatic alcohols, in accordance with the stability of the leaving aryloxy anions. The rate of displacement<sup>478</sup> can even be correlated with *pK* values<sup>479</sup> of the corresponding phenols. Displacement of the *p*-nitrophenoxy group at 20° in alkaline methanol is about 16 times more rapid than of the phenoxy group in 2,4-dinitrophenyl aryl ethers. Hydrolysis of *symm*-2,4-dinitrophenyl ether<sup>480,481</sup> and other activated ethers<sup>482</sup> can be effected by boiling with 20% alcoholic potassium hydroxide. With more heavily nitrated aromatic ethers and hydroxide ion complex side reactions are often encountered.

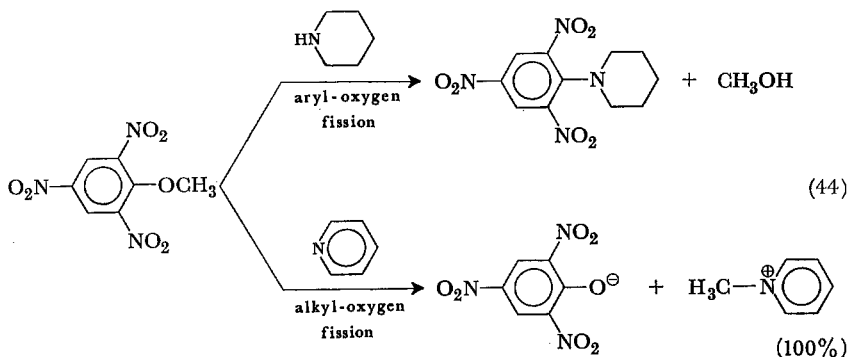
The concept of acidity functions has been applied to the reaction of 2,4-dinitroanisole in strongly alkaline media<sup>483-485</sup>.

#### 4. Displacement of alkoxy- and aryloxy groups by amines

Displacement of the methoxy group in 2,4-dinitroanisole or methyl picrate by alcoholic ammonia<sup>486,487</sup> or aniline<sup>477</sup> is difficult partly because of side reactions. Displacement of phenoxy groups is easier e.g. 2,4-dinitrodiphenyl ether upon boiling with aniline gives 2,4-dinitrodiphenylamine in 80 % yield<sup>477,488</sup>. With alcoholic ammonia phenoxy displacement is much slower<sup>489</sup>. Even a single nitro group in the 2-position of diphenyl ether may activate the ether linkage sufficiently for cleavage by certain nucleophiles such as hydrazine<sup>478</sup> to give benzotriazole by further reduction and condensation.

In the nucleophilic reaction of amines with asymmetric diphenyl ethers containing several nitro groups the amine nitrogen becomes attached to the more heavily nitrated ring and the second ring is isolated as a phenol. This has been shown by Turner<sup>490-492</sup> for many reactions with piperidine. Other examples have been reviewed by Ungnade<sup>493</sup>. Displacement of aryloxy groups by pyridine and diethylamine has been reported by Beckwith and Miller<sup>130</sup>.

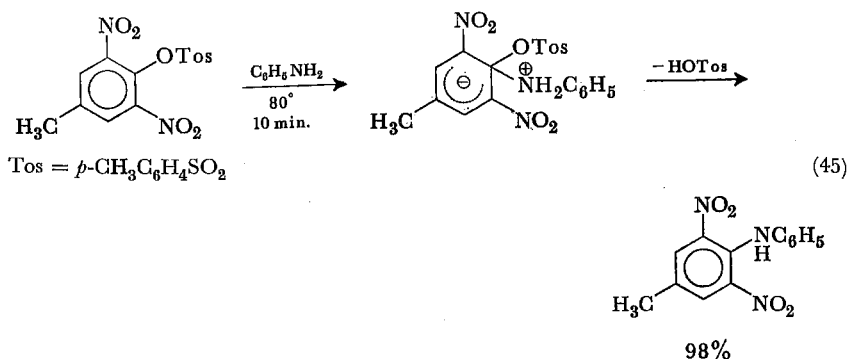
The reactivity for replacement in 4-nitro- and 3,4-dinitrophenyl-oxo-, thio- and seleno ethers by amines decreases in the order<sup>494</sup>  $O > S \sim Se$ . Finally it should be pointed out that the cleavage of activated aryl *alkyl* ethers does not always proceed via Meisenheimer type complexes. Especially tertiary amines (pyridine, dimethylaniline, trialkylamines) attack di- and trinitroanisoles not at the aromatic nucleus but at the aliphatic methyl group in a  $S_N2$  type aliphatic substitution<sup>495-497</sup> leading to quarternary ammonium salts (equation 44),



Primary and secondary amines can form Meisenheimer complexes with an intramolecular hydrogen bond (cf. section II.2). This may

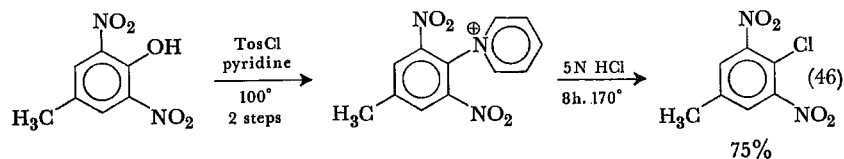
well be the dominant factor which leads to a different pathway with tertiary amines, where hydrogen bonds play no role.

An indirect way of displacing a hydroxyl group from nitrophenols goes by way of the tosylate, easily accessible by reaction of the phenol with tosyl chloride. The strong electron withdrawing power of the sulphonyl group makes the tosylate an excellent leaving group in nucleophilic displacement by amines<sup>498-500</sup> (equation 45),



With tertiary amines (pyridines, *N,N*-dialkylanilines) the displacement follows in principle the same course<sup>501,502</sup>.

A complication arises when the tosylate is prepared *in situ* from *tosyl chloride* and (polynitro)-phenol in pyridine solution. The solvent displaces the tosylate group but the resulting pyridinium salt is further attacked by weakly nucleophilic chloride ion, set free during the esterification. This illustrates the high leaving tendency of pyridine from nitroaryl pyridinium salts. The whole sequence of reactions constitutes a practical procedure for replacement of a hydroxyl group by chlorine, especially when hydrochloric acid is added in the final step<sup>501,502</sup> (equation 46),



In the absence of pyridine no such products but only the trinitrophenyl tosylate is obtained because chlorine cannot displace the tosylate group. Accordingly lithium chloride fails to react with 2,4-dinitrophenyl tosylate<sup>502</sup>.

TABLE 43. Displacement of alkoxy and aryloxy groups by amines and mercaptides.

Position of NO <sub>2</sub> group	Alkoxy and aryloxy groups	Reagent	Solvent	Ref.
1-NO <sub>2</sub>	4-OMe	piperidine	DMSO	114
	4-OPh	H <sub>2</sub> NNH <sub>2</sub> , piperidine, aniline	EtOH; DMSO	114, 494
	4-OAr	H <sub>2</sub> NNH <sub>2</sub> , piperidine, aniline	EtOH	494
	4-OAr	piperidine	DMSO	114
	1-OH	R <sub>4</sub> N <sup>+</sup> NO <sub>3</sub> <sup>-</sup>		348, 349
	1-OMe	KOH, RSH	EtOH	240
	1-OMe	piperidine	MeOH	293
	1-OMe	piperidine	aq. dioxan	78
		MeS <sup>-</sup>	dioxan, DMF, MeOH	159, 249
	3-OMe	NH <sub>3</sub> liq.		216
	1-OR <sup>a</sup>	NH <sub>3</sub> liq.		216
	6-OR	NH <sub>3</sub> liq.		216
	1-OPh	piperidine	aq. dioxan	293, 383
	1-OPh	piperidine	aq. dioxan	78
2,4,6	1-OPh	piperidine	benzene	92
	1-OC <sub>6</sub> H <sub>3</sub> -2,4-(NO <sub>2</sub> ) <sub>2</sub>	piperidine	aq. dioxan	78
	1-OC <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub>	piperidine	aq. dioxan	68, 78
		piperidine	MeOH	67
		PhS <sup>-</sup>	MeOH	70
		aromatic amines		433
	1-OH	NH <sub>3</sub> liq.		226
	1-OR	POCl <sub>3</sub> + pyr., HCl + pyr. <sup>b</sup>		471, 472
	1,3-(OH) <sub>2</sub>	POCl <sub>3</sub>		
		ethanolamine		365
		NH <sub>3</sub>	MeOH	503

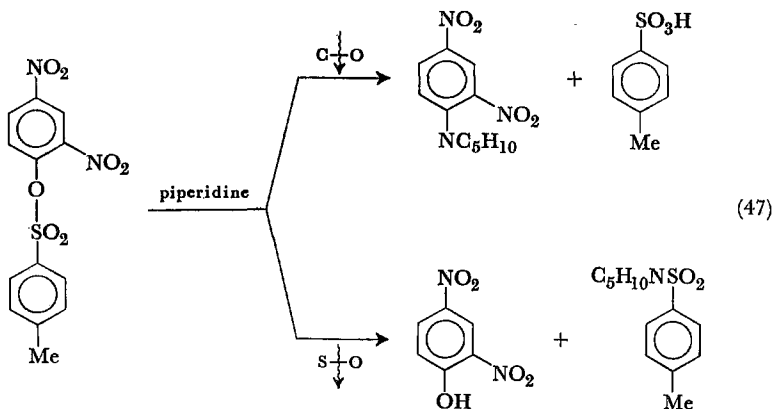
<sup>a</sup> R = alkyl.<sup>b</sup> pyridine.

Neither does sodium phenoxide give a diphenyl ether with an aryl tosylate. It reacts with 2,4-dinitrophenyl tosylate predominantly by nucleophilic attack on sulphur, yielding phenyl tosylate and 2,4-dinitrophenol (trans-esterification)<sup>502</sup>.

A survey of further examples of reactions between amines and activated ethers is given in Table 43.

## 5. Displacement of sulphonate ( $\text{OSO}_2\text{Ar}$ ) and other ester groups

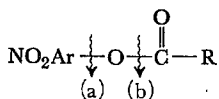
Removal of a sulphonate group from an aromatic molecule under the activating influence of a nitro group offers two possibilities, C—O or S—O fission (equation 47).



With reagents of high polarizability (e.g.  $\text{PhS}^-$ ) C—O fission takes place predominantly<sup>74</sup>. Introduction of methyl groups in the *ortho* positions of the arylsulphonyl groups gives no indication of a steric influence on the relative proportions of C—O vs S—O fission<sup>74,75</sup>.

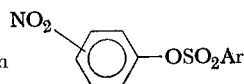
In 2,4-dinitronaphthalenes the *p*-toluenesulphonate group is displaced from the 1-position even faster than fluorine<sup>67</sup>. Examples of reactions of sulphonate displacement are collected in Table 44.

Similarly carboxylic esters (Table 45) offer two modes of fission:



an Ar—O fission (a) or an acyl—O fission (b). Mostly acyl—O fission predominates, but for trinitrophenyl benzoate in neutral

TABLE 44. Nucleophilic displacement of sulphonate groups from



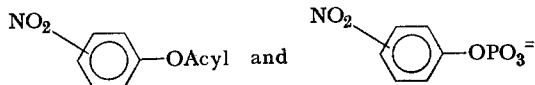
Position of NO <sub>2</sub> group	Sulphonate	Reagent	Solvent	Ref.
1	2- <i>p</i> -toluene	piperidine	aq. dioxan	74, 75
	4- <i>p</i> -toluene	piperidine, PhS <sup>-</sup>	aq. dioxan	74, 75
	4- <i>p</i> -toluene	piperidine	DMSO	114
	4- <i>p</i> -toluene	acetoacetic ester	THF	74
	2-mesitylene	piperidine	aq. dioxan	74, 75
	4-mesitylene	piperidine	aq. dioxan	74, 75
1,3	4- <i>p</i> -toluene	MeOH + base		504
2,4	1- <i>p</i> -toluene	PhS <sup>-</sup>	aq. dioxan	74
	1- <i>p</i> -toluene	R <sub>4</sub> <sup>a</sup> N <sup>+</sup> NO <sub>3</sub> <sup>-</sup>		348
	1- <i>p</i> -toluene	piperidine, aniline, glycine ethyl ester, MeO <sup>-</sup> , PhO <sup>-</sup>	several	67, 74, 75
	1-mesitylene	piperidine	MeOH	75
	1-mesitylene	piperidine	several	74
		MeO <sup>-</sup>	acetone-MeOH	74

<sup>a</sup> R = alkyl.

methanol<sup>504,505</sup> and for *p*-nitrophenyl acetate<sup>114</sup> in DMSO Ar-O fission is reported.

The relative importance of C—O splitting in nitrophenyl phosphates (cf. Table 45) and sulphates<sup>506</sup> depends among other things upon the nature of the amine used<sup>298,507</sup>.

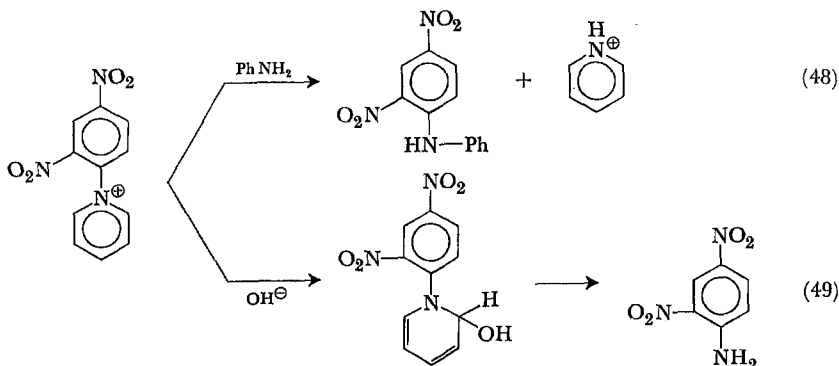
TABLE 45. Displacement of ester groups from



Position of NO <sub>2</sub> group	Ester group	Reagent	Solvent	Ref.
1	4-OOCCH <sub>3</sub>	piperidine	DMSO	114
	4-OPO <sub>3</sub> <sup>2-</sup>	sec. and prim. amines	H <sub>2</sub> O	298, 507
	4-OSO <sub>3</sub> <sup>-</sup>	amines	H <sub>2</sub> O	506
2,4	1-OOCMe	NH <sub>3</sub> liq.		216
	1-OOCPh	NH <sub>3</sub> liq.		216
2,4,6	1-OOCPh	MeOH + base		505
	1-OOCMe	MeOH + base		505

## 6. Displacement of amino and ammonium groups

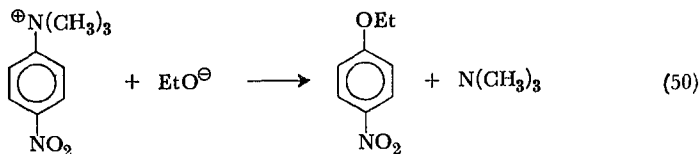
In section IV.4 it was shown that in 2,4-dinitrophenyl pyridinium salts the pyridine group is highly mobile and readily displaced by weakly nucleophilic chloride ion. Accordingly stronger nucleophilic aniline yields 2,4-dinitrodiphenylamine<sup>508</sup> (equation 48) but hydroxide ion does not give 2,4-dinitrophenol. Instead an unstable addition product is formed, in which hydroxide ion has broken up the electron-sextet of the pyridine ring. The adduct undergoes ring fission to an unsaturated highly colored aldehyde<sup>509</sup>, which plays an essential part in providing a C<sub>5</sub>-moiety for an elegant azulene synthesis<sup>510</sup> (equation 49),

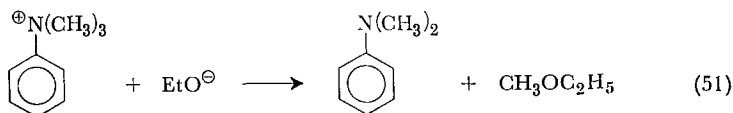


+ destruction of the pyridine ring to a C<sub>5</sub>-fragment.

On the other hand *N*-alkyl- and *N,N*-dialkyl-2,4-dinitroaniline<sup>511</sup>, when heated with alkali are hydrolysed to 2,4-dinitrophenol and amine. Mechanistically similar trans-aminations in nitro-activated aromatic amines have also been observed<sup>512</sup>. One single nitro group activates a trimethylamino group in the *para* position sufficiently to be displaced by the ethoxyl group in refluxing ethanol<sup>513</sup> (equation 50).

It is of interest to note that similar treatment of non-activated aryltrimethylammonium compounds leads to demethylation<sup>513,514</sup> with formation of methyl ethyl ether (equation 51),





In contrast to tertiary amino groups, primary amino groups are displaced far more difficultly, because of highly complex side reactions.

For further examples of these and other amine displacements the reader is referred to Table 46.

TABLE 46. Displacement of amino groups.

Position of NO <sub>2</sub> group	Amino substituent	Reagent	Solvent	Ref.
1	4-NH <sub>2</sub>	OH <sup>-</sup>	H <sub>2</sub> O	483
2,4	1-NH <sub>2</sub>	MeO <sup>-</sup>	MeOH—DMSO	206, 209
	1-NH <sub>2</sub>	MeO <sup>-</sup>	DMSO	197
	1-NH <sub>2</sub>	RO <sup>-a</sup>	ROH <sup>a</sup>	515
	3-NH <sub>2</sub>	MeO <sup>-</sup>	MeOH—DMSO	206
	3-NH <sub>2</sub>	NH <sub>3</sub> liq.		216
	6-NH <sub>2</sub>	NH <sub>3</sub> liq.		216
	1-NPhH	OH <sup>-</sup>	H <sub>2</sub> O	384
	1-NHPh	MeO <sup>-</sup>	MeOH—DMSO	197, 206, 209
	1-NHPh	RO <sup>-</sup>	ROH	515
	1-NMe <sub>2</sub>	MeO <sup>-</sup>	DMSO	205
	1-NR <sub>1</sub> R <sub>2</sub> <sup>a</sup>	NH <sub>3</sub> liq.		216
	1-pyridinium	PhS <sup>-</sup>	MeOH	70
2,4,6	1-NH <sub>2</sub>	OH <sup>-</sup> ; MeO <sup>-</sup>	H <sub>2</sub> O; MeOH	198, 199, 203
	1-NH <sub>2</sub>	EtO <sup>-</sup>	EtOH	429
	1-NH <sub>2</sub>	ethanolamine		365
	1-NHR	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	503
	1-NMc <sub>2</sub>	OH <sup>-</sup> ; MeO <sup>-</sup> ; CH <sub>3</sub> COCH <sub>2</sub> <sup>⊖</sup>	H <sub>2</sub> O; MeOH NEt <sub>3</sub> + acetone	198, 203 226
	1-NR <sub>2</sub>	OH <sup>-</sup>	DMSO—H <sub>2</sub> O	206
	1-NR <sub>2</sub>	MeO <sup>-</sup>	MeOH; DMSO	206, 209, 375
	1-NR <sub>1</sub> R <sub>2</sub>	NH <sub>3</sub> liq.		216
	1,3,5-(NH <sub>2</sub> ) <sub>3</sub>	NH <sub>3</sub> liq.		216
	1-NMeNO <sub>2</sub>	NaOH	H <sub>2</sub> O	314

<sup>a</sup> R, R<sub>1</sub>, and R<sub>2</sub> = alkyl.

## 7. Displacement of miscellaneous groups

In this section are collected displacement reactions of various groups (Table 47) from nitro activated aromatic systems by a variety of nucleophilic reagents.



TABLE 47. Miscellaneous reactions of activated nitroaromatic compounds with nucleophilic reagents.

Position of NO <sub>2</sub> group	Substituents	Reagent	Solvent	Ref.
1	4-N <sub>3</sub>	MeO <sup>-</sup>	MeOH	153
	4-SO <sub>3</sub> H	NaOH	H <sub>2</sub> O	516
	4-SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>p</i> -NO <sub>2</sub>	piperidine	DMSO	114
	4-SO <sub>2</sub> Ph	piperidine	DMSO	114
	4-CN	piperidine	DMSO	114
	4-SAr; 4-SeAr	hydrazine, piperidine, aniline	EtOH	494
2,4	2-SCH <sub>2</sub> CH <sub>2</sub> OH	none		517
	4-SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -NO <sub>2</sub>	piperidine	DMSO	114
	4-SPh	piperidine	DMSO, aq. dioxan	78, 114
	1-Ph	NH <sub>3</sub> liq.		216
	6-COOH	NH <sub>3</sub> liq.		216
	1-SO <sub>2</sub> R	RSH		345
	1-SO <sub>2</sub> Me	SO <sub>3</sub> <sup>=</sup>	MeOH	
	1-SO <sub>3</sub> <sup>-</sup>	MeO <sup>-</sup>	dioxan, DMF, MeOH	249
	1-SO <sub>2</sub> Ph	piperidine PhS <sup>-</sup>	dioxan, DMF, MeOH	249
	1-SOPh	piperidine PhS <sup>-</sup>	aq. dioxan MeOH	67, 68, 70
2,6	1-N <sub>3</sub>	MeO <sup>-</sup> MeS <sup>-</sup>	MeOH	67, 70
	1-SMe	NHMe <sub>2</sub>	MeOH	159
	1-SO <sub>2</sub> R <sup>a</sup>	NH <sub>3</sub> ; MeNH <sub>2</sub> ; EtNH <sub>2</sub> ; PhCH <sub>2</sub> NH <sub>2</sub> ; anilines	dioxan, MeOH, DMF	249
3,5	1-SO <sub>3</sub> H	creatinine, allethrine, diethylpiperidine	several	345
2,4,6	1-Me	NaOH	H <sub>2</sub> O	518
	1-Me	MeO <sup>-</sup>	H <sub>2</sub> O	314
	1-Me	pyridine	MeOH	212
				362, 364

1-Me	anilines	361
1-Me	ethanolamine	365
1- <i>t</i> -Bu	ethanolamine	365
1-Me	EtO-	429
1,3-Me <sub>2</sub>	NH <sub>3</sub> liq.	216
1,3-Me <sub>2</sub>	EtO-	429
1-R	NH <sub>3</sub> liq.	216
1-N <sub>3</sub>	MeO-	153
1-SO <sub>3</sub> H	amines, amino acids	519
1-SO <sub>2</sub> Ar	RO- <sup>a</sup>	343
1-SO <sub>2</sub> Ph	amines mercaptides	343
	MeO-	
	EtOH	
	EtOH	
	MeOH	
	ROH <sup>a</sup>	
	EtOH	

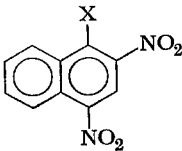
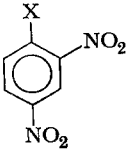
<sup>a</sup> R = alkyl.

## V. DISPLACEMENTS IN POLYCYCLIC AND HETEROCYCLIC NITRO COMPOUNDS

### I. Displacements in polycyclic nitro compounds

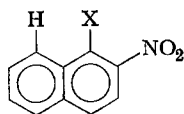
Elias and Parker<sup>282</sup> have given a comparative literature survey of nucleophilic displacement reactions for a number of analogous nitrobenzene and nitronaphthalene derivatives, the only polycyclic nitroaromatic system studied to some extent. In hydroxylic solvents the nitronaphthalenes seem to have a lower energy of activation<sup>30,186,282</sup>. It is thought that for naphthalenes the two-stage mechanism is more pronounced. Table 48 illustrates the higher

TABLE 48. Comparison of the rate of halogen displacement from 1-X-2,4-dinitrobenzene and 1-X-2,4-dinitronaphthalene by aniline in ethanol at 50°.

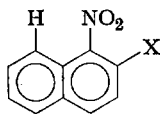
	X:	I	Br	Cl	F
	$10^4 \times k_2$ :	224			
	$k_{rel}$ :	1.00	2.18	2.01	8.52
	$10^4 \times k_2$ :	1.31			
	$k_{rel}$ :	1.00	3.10	2.05	128

reactivity of 1-X-2,4-dinitronaphthalene in comparison with 1-X-2,4-dinitrobenzene. Remarkable in this respect is the relatively low reactivity of fluorine. However, the order of reactivities of halogens in the naphthalene series is similar to that in the benzene series<sup>395</sup> (cf. section III.7, Table 28).

In nitronaphthalenes there is a marked difference in reactivity between the two isomers **5** and **6**.



(5)



(6)

TABLE 49. Some displacement reactions of nitronaphthalenes and nitroanthracenes.

Naphthalene substrate	Reagent	Solvent	Ref.
1-F-2,4-(NO <sub>2</sub> ) <sub>2</sub>	aniline	ethanol	282
1-Cl-2-NO <sub>2</sub>	KOH	aq. dioxan	182, 185
	KOH	aq. ethanol	184, 185
	MeO <sup>-</sup>	MeOH	183
	EtO <sup>-</sup>	EtOH	183
	piperidine	benzene, EtOH	187
		piperidine	395
1-Cl-4-NO <sub>2</sub>	KOH	aq. dioxan	182, 185
		aq. ethanol	184, 185
	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	183, 190
	piperidine	EtOH	187, 190
		benzene	186
		aq. EtOH	184, 185
2-Cl-1-NO <sub>2</sub>	KOH	aq. dioxan	182, 185
	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	183
	piperidine	piperidine	395
		EtOH; benzene	188, 190
1-Cl-2,4-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	189, 190
	NH <sub>3</sub>	MeOH	520
	piperidine	benzene; EtOH	186, 189, 190
	aniline	EtOH, MeOH	282, 520
	PhSO <sub>2</sub> H + NaHCO <sub>3</sub>	acetone	344
	<sup>a</sup> (RO) <sub>2</sub> P(O)SNa	EtOH	522
1-Cl-4,8-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup>	MeOH	521
1-Cl-4,5-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	189, 190
	piperidine	EtOH and PhH	186, 189, 190
1-Cl-2,4,5-(NO <sub>2</sub> ) <sub>2</sub>	aniline	EtOH	282
1-Br-2-NO <sub>2</sub>	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	188, 190
	piperidine	EtOH	188, 190
		piperidine	395
		benzene	186, 521
1-Br-4-NO <sub>2</sub>	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	188, 190
	piperidine	EtOH	188, 190
		benzene	186
1-Br-8-NO <sub>2</sub>	piperidine	benzene	521
2-Br-1-NO <sub>2</sub>	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	188
	piperidine	EtOH, benzene	188
		piperidine	395
1-Br-2,4-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	189, 190
	NH <sub>3</sub>	MeOH	520
	piperidine	EtOH; benzene	186, 189, 190
	aniline	EtOH; MeOH	282, 520
1-Br-4,5-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup> ; EtO <sup>-</sup>	MeOH; EtOH	189, 190
	piperidine	EtOH; benzene	186, 189, 190

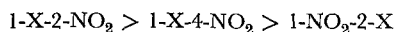
(continued)

TABLE 49. (continued)

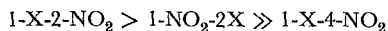
Naphthalene substrate	Reagent	Solvent	Ref.
1-I-2-NO <sub>2</sub>	piperidine	piperidine	395
2-I-1-NO <sub>2</sub>	piperidine	piperidine	395
1-I-2,4-(NO <sub>2</sub> ) <sub>2</sub>	NH <sub>3</sub>	MeOH	520
	aniline	EtOH; MeOH	282, 520
1-NO <sub>2</sub>	Me <sub>2</sub> <sup>⊕</sup> SOCH <sub>2</sub> <sup>⊖</sup>	DMSO	418
1,3-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup>	DMSO; acetone	226
1-OH-2-NO <sub>2</sub>	KOH	MeOH	243
1-OMe-4-NO <sub>2</sub>	KOH	ROH	243
2-OMe-1-NO <sub>2</sub>	KOH	ROH	243
1-OMe-2,4-(NO <sub>2</sub> ) <sub>2</sub>	ROH + KOH	<sup>a</sup> ROH benzene	243
	MeO <sup>-</sup>	DMSO	226
1-SO <sub>2</sub> Ph-4-OMe-2-NO <sub>2</sub>	aniline	aniline	344
	NH <sub>3</sub>	EtOH	344
1-SO <sub>2</sub> Ph-2,4-(NO <sub>2</sub> ) <sub>2</sub>	MeO <sup>-</sup>	MeOH	344
	piperidine; arom.		
	amines	dioxan	344
	thiophenols	dioxan	344
anthracene substrate			
9-NO <sub>2</sub>	MeO <sup>-</sup>	DMSO	226
9-OMe-10-NO <sub>2</sub>	MeO <sup>-</sup>	DMSO	226

<sup>a</sup> R = alkyl.

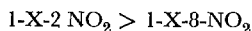
For X = Cl, Br or I the 2-X-isomer has a lower reactivity in piperidino-dehalogenation<sup>182-184,188,189,395</sup>. This effect is ascribed mainly to the (extra) steric hindrance by the hydrogen in 8-position which forces the 1-nitro group out of the 'aromatic plane' and thus lowers its activating power (cf. section III.6). However, this view is not always supported by experiment<sup>520</sup>. According to Simonetta and Favini<sup>185</sup> electronic effects also decrease the reactivity of the 1-NO<sub>2</sub>-2-X-isomer. For mononitronaphthalenes the order of reactivity (X = Br or Cl) for reactions of MeO<sup>-</sup>, EtO<sup>-</sup> and piperidine in methanol or ethanol is given by Beltrame and Simonetta<sup>188</sup> as:



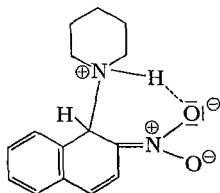
while for piperidine in benzene the sequence is:



and<sup>521</sup>



There is a strong *ortho* effect analogous to the built in solvation effects for the benzene compounds for reactions with prim. or sec. amines.



Introduction of a second nitro group shows a strong increase of reactivity for the 1-X-2,4-dinitro isomers, similar to the benzene series. However, a second nitro group for instance in the 5-position, i.e. 1-X-4,5-dinitronaphthalenes, gives an increase of only 5- to 30-fold<sup>189</sup>. Similar findings are reported by Elias and Parker<sup>282</sup>.

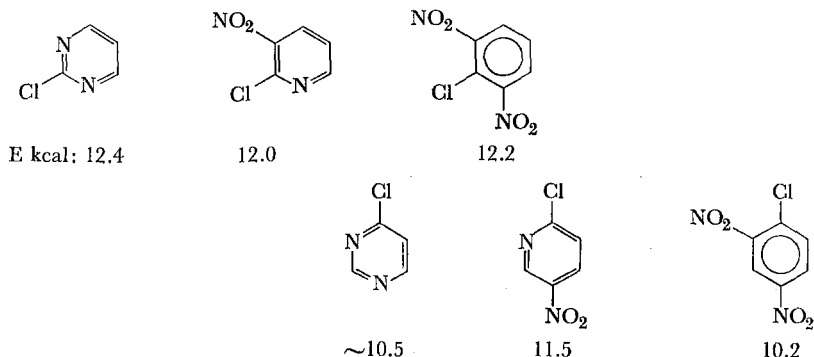
## 2. Displacements in heterocyclic nitrocompounds

Nucleophilic substitution in heteroaromatic compounds has been reviewed recently in an excellent way by Illuminati<sup>14</sup>. Sheperd and Fredrick<sup>16</sup> and by Mertel<sup>523</sup>. A hetero atom introduces a strong perturbation in the electron densities as compared with the homoaromatic system<sup>87</sup>. In pyridine systems for instance the nitrogen atom exerts a strong activation. Thus pyridine behaves in many aspects analogous to nitrobenzene<sup>524</sup>. This activation is enhanced<sup>154</sup> in the *N*-oxide ( $>\overset{\oplus}{\text{N}}-\overset{\ominus}{\text{O}}$ ) and even more by  $>\overset{\oplus}{\text{N}}-\text{Me}$ . The role of the nitro group as an activating substituent is somewhat less prominent in a pyridine- than in a benzene ring.

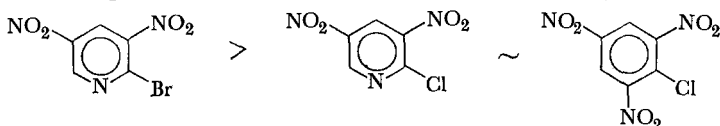
Apart from a structural difference of the aromatic molecules the anilino-dechlorination of 3-nitro-6-chloropyridine by a number of substituted anilines gives a Hammett relation with a  $\rho$ -value fully comparable to the values found in the homocyclic series<sup>81</sup> (section III.5).

The *ortho/para* reactivity ratio for displacement of halogen from the *ortho*- and *para*-position are similarly comparable<sup>81,82</sup> (section II.2). The leaving aptitude of halogens is also similar to that for the homocyclic series<sup>525</sup>. Nitro groups are easily displaced from heterocyclic systems<sup>154,177,526,527</sup>. The rates for mononitropyridine and for dinitrobenzene compounds do not differ appreciably<sup>82</sup>. This result

also follows on comparing the energy of activation for the replacement of chlorine<sup>84</sup>:

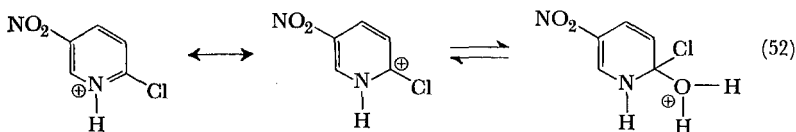


Another comparison of relative reactivities is given by Talik<sup>299</sup>:



Mariella and coworkers<sup>528</sup> report the development of colors in the reactions of alkoxides with halopyridines presumably associated with intermediate complexes as also noticed with analogous homocyclic compounds.

Nucleophilic substitution in pyridines is catalyzed in acidic media<sup>387</sup> and this has been ascribed to exalted activation by protonation of the N-atom (equation 52).



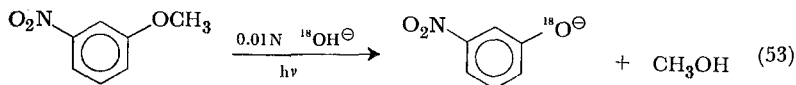
Amino-dehalogenations from 4-halo-5-nitropyrimidines are easily effected<sup>529-531</sup>. Nucleophilic displacements from quinolines<sup>532,533</sup>, pyridines<sup>14,16,523,527,534,533,535</sup> and pyridine- and quinoline-N-oxides<sup>536-538</sup> have been studied by several authors.

## VI. NUCLEOPHILIC PHOTOSUBSTITUTION

### I. Photochemical displacement of alkoxy groups

About 13 years ago it was discovered<sup>266</sup> by chance that an alkaline solution of *m*-nitrophenyl phosphate is hydrolyzed in light much

more rapidly than in the absence of light. A similar effect is found for *m*-nitroanisole. The aryl-oxygen bond is broken as shown by a tracer experiment<sup>272</sup> (equation 53).



Closer U.V.-spectroscopic investigation at various time intervals (cf. Figure 6) shows four isobestic points, an impressive illustration

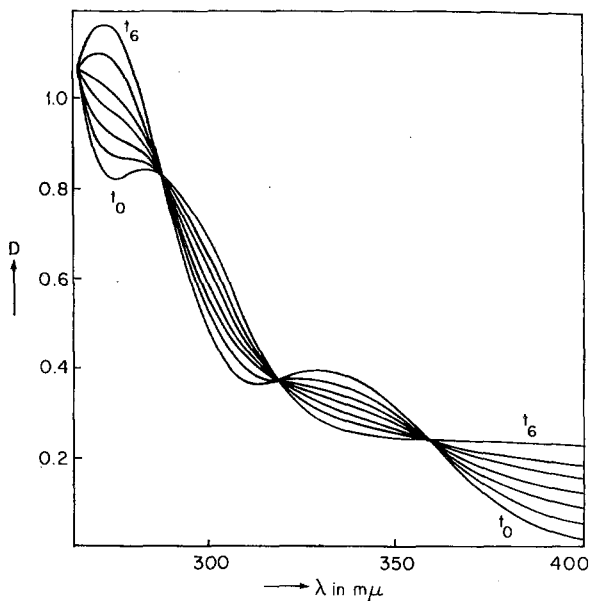
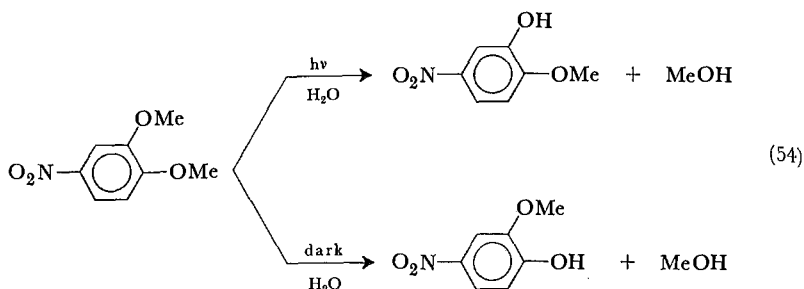


FIGURE 6. Absorption spectrum of *m*-nitroanisole in 0.010 *N*NaOH in water during irradiation with light of  $\lambda = 313 \mu\text{m}$ .

of the absence of aromatic byproducts, the sole reaction products being *m*-nitrophenol and methanol. A remarkable feature in these photochemical reactions is the specific *meta* activation, in contrast to the known *ortho/para* activation of the nitro group in ordinary 'dark' reactions (cf. section II.1). The difference in 'light' and 'dark' activation by the nitro group is demonstrated elegantly in the selective hydrolysis of 4-nitroveratrole<sup>268</sup> (equation 54).

Recently Havinga<sup>269</sup> has reviewed the photochemical reactions of nitrophenyl esters (phosphates<sup>266,539-541</sup> and sulphates<sup>266</sup>), and



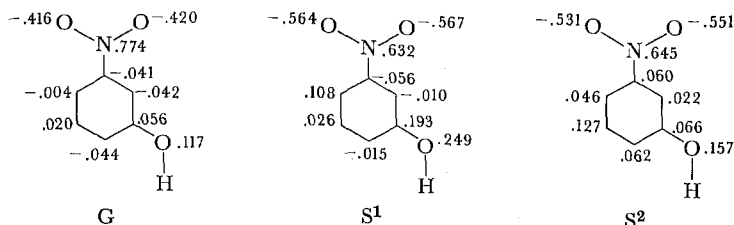


nitrophenyl ethers (methyl<sup>268,540</sup>), ethyl<sup>268</sup>, propyl<sup>268</sup>, allyl<sup>271</sup>, and triphenyl<sup>268</sup>) with a variety of nucleophiles ( $\text{OH}^\ominus$ <sup>272</sup>,  $\text{H}_2\text{O}$ <sup>272</sup>,  $\text{CH}_3\text{NH}_2$ <sup>273,276</sup>,  $(\text{CH}_3)_2\text{NH}$ <sup>273</sup>, and  $\text{HCl}$ <sup>542</sup>). Introduction of one more nitro group at any position in *m*-nitroanisole favors the quantum yield  $\phi$ , all (four) dinitroanisoles undergoing photohydrolysis in alkaline medium with  $\phi = 0, 30 - 0, 45$ <sup>268</sup>.

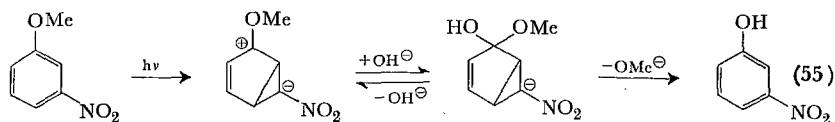
Photosubstitutions of *m*-nitrophenyl esters and ethers show the following characteristics<sup>269,539,540</sup>:

- (1) Oxygen has little or no influence, therefore a homolytic reaction seems highly improbable.
- (2) The temperature coefficient is negligible.
- (3) The degree of conversion is proportional to the amount of light absorbed by the substrate, and the reaction is zero order in ester or ether.
- (4) With *m*-nitrophenyl sulphate the quantum yield is constant in the pH range 2–14. Protonation or deprotonation is therefore not essentially involved.
- (5) Over a broad spectral region quantum yields are practically independent of the wavelength e.g.  $\phi = 0.20\text{--}0.22$  from 250–350  $\mu\text{m}$  for the photohydrolysis of *m*-nitroanisole in 0.010 *N*NaOH solution<sup>269</sup>. At longer wavelengths quantum yields decrease.

Particularly these last observations suggest that photosubstitution takes place via a  $\pi \rightarrow \pi^*$  excited singlet state<sup>543</sup>. Theoretical calculations<sup>265</sup> for *m*-nitro isomers have shown that in the first excited state ( $S^1$ ), the positive charge density at the carbon atom carrying the ether or ester function is considerably higher than in the ground state (G) or the second excited state ( $S^2$ ). This renders the first excited state of *m*-nitroanisole, (corresponding with  $\lambda_{\text{max}} = 330 \mu\text{m}$  in the U.V. spectrum of Figure 6 at  $t = 0$ ) highly susceptible to



nucleophilic attack. In a crude but convenient symbolism the photochemical reaction can be depicted as in equation 55.



That light of shorter wavelength is photochemically equally active can be explained by radiationless transition from the second excited singlet state ( $\lambda_{\max} = \sim 274 \mu\text{m}$ ) to the first. The decrease of quantum yields at wavelength  $> 350 \mu\text{m}$  is also logical because in this region the  $n \rightarrow \pi^*$  transition becomes important, and this leads to a lower excited state, with charge distributions unfavorable for nucleophilic attack. The short life time of the first excited singlet state of *m*-nitroanisole ( $10^{-7}$ – $10^{-9}$  sec) is probably compensated by its high reactivity. A rough estimate at least indicates that collision frequencies are high enough to allow reaction of the excited substrate with a nucleophile, provided it is present in sufficiently high concentration. For instance it has been found that concentrations of  $10^{-1}$  molar or higher are required for nucleophiles such as methylamine and pyridine whereas for hydroxyl ions with their greater mobility, concentrations of  $10^{-2}$  molar are sufficient for optimum quantum yields.

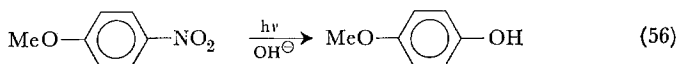
## 2. Photochemical displacement of halogen

Because halogens are displaced more easily in nucleophilic aromatic substitutions than alkoxy groups it might be expected that 3-nitrohalobenzenes are suitable substrates in photochemical substitutions. Experimentally however, no photosubstitution by hydroxyl ion has been observed<sup>274</sup> with 3-nitrobromobenzene or with 3,5-dinitrobromobenzene. This may be associated with the tendency of bromo compounds to promote transitions to (unreactive) triplet states.

On the other hand in 2-chloro- and 2-bromo-4-nitroanisoles the halogen atom can be replaced by a hydroxyl group in 44–48 % yield upon irradiation<sup>274</sup>. U.V. spectra at various degrees of conversion show again isobestic points. So far this seems the only instance in photochemical nucleophilic halogen displacement.

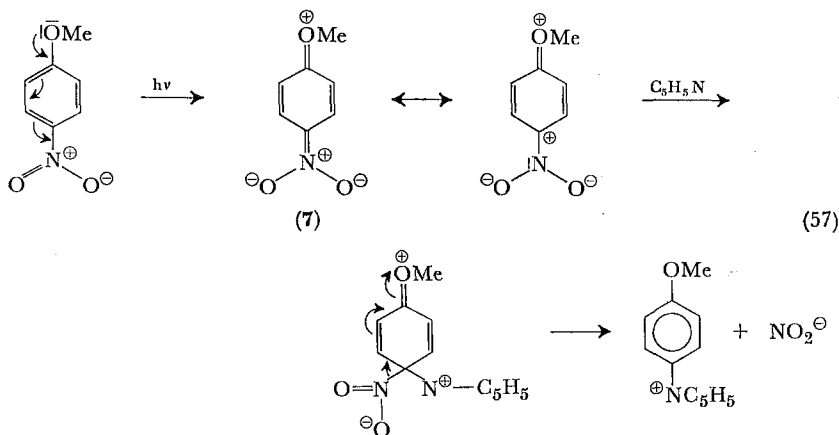
### 3. Photochemical displacement of nitro groups

When *p*-nitroanisole is subjected to photohydrolysis in a weakly alkaline medium only small amounts of *p*-nitrophenol are formed, the main product being *p*-methoxyphenol (product ratio 1:4)<sup>539</sup>. Apparently hydroxyl ion replaces the nitro group in preference to the methoxy group (equation 56). In somewhat stronger alkaline solution (0.1 N) Havinga *et al.* have noticed formation of oxydation products<sup>271</sup>. This complication is absent in the reaction of *p*-nitro-



anisole and *p*-nitrophenyl phosphate with pyridine<sup>540</sup>. This nucleophile acts highly selective with exclusive displacement of the nitro group thus yielding an arylpyridinium nitrite as the sole product (equation 57).

Letsinger<sup>540</sup> has argued that **7** is an important resonance hybrid for the excited state of *p*-nitroanisole in accordance with molecular orbital calculations<sup>544</sup>.



This mechanism differs from conventional nucleophilic displacements in that the bonding pair of electrons between the nitro group and the aromatic ring returns to the ring rather than departing with the leaving group.

Under the same conditions photoexcited *p*-nitrophenol does not undergo substitution by pyridine, and this has been ascribed to the net negative charge of the excited phenoxide ion, which would lower its electrophilic character. Interestingly isoelectronic 4-nitropyridine N-oxide with no net charge has been reported to lose nitrite ion with piperidine<sup>545</sup>, in a process accelerated by light. In photochemical displacements of nitro groups by pyridine an electron donating *para*-substituent is essential, no photochemical reaction being observed with nitrobenzene, *p*-dinitrobenzene or *m*-nitroanisole.

There is no certainty whether this lack of reactivity is caused by unfavorable charge distribution in excited states or by a substituent effect on the lifetimes of excited states. With kinetic and spectral data Gold and Rochester<sup>196-204</sup> showed that the photoinduced liberation of nitrite ion from trinitroaromatics such as methyl picrate, picric acid and picramide in methanol solutions of sodium methoxide, and from trinitrobenzene in aqueous solutions of sodium hydroxide, involves formation of a 1:1 complex. On absorption of light this—and not the excited trinitroaromatic—reacts with a second equivalent of base. In reactions of mononitroaromatics with pyridines there are no indications for reactions between substrate and nucleophile prior to photoexcitation.

Irradiation of 2,4,6-trinitrotoluene<sup>546</sup> and 1,3,5-trinitrobenzene<sup>547</sup> effects changes in the UV and ESR spectra of these compounds, but nothing is known about the chemical changes which these molecules have undergone.

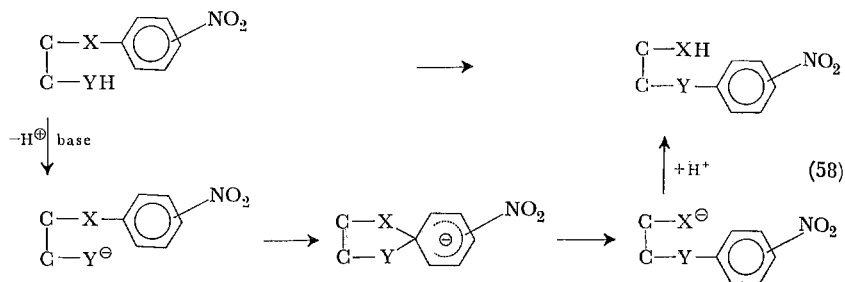
## VII. REARRANGEMENT REACTIONS

### I. Smiles rearrangement

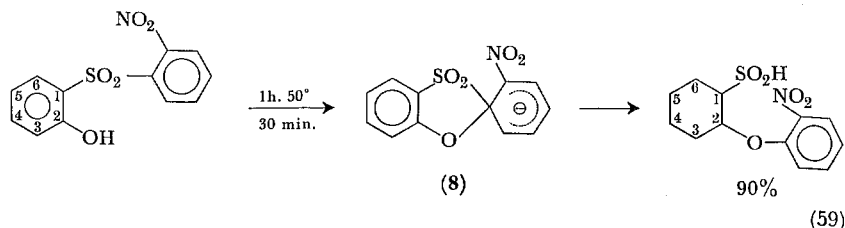
The Smiles rearrangement can be regarded as an intramolecular nucleophilic aromatic substitution as shown in equation 58.

The atoms on the bridge between X and Y are often part of a second aromatic nucleus but can also belong to an aliphatic chain.

As the scheme suggests, X should be a good leaving group and  $Y^{\ominus}$  (or YH) a nucleophile. These requirements are illustrated in



the typical rearrangement—discovered by Smiles<sup>548</sup>—of a diaryl-sulfone ( $X = SO_2$ ) suitably substituted by a hydroxyl group



( $=YH$ ) and a nitro group. The main product is a sulphinic acid of a nitro substituted diphenyl ether (equation 59).

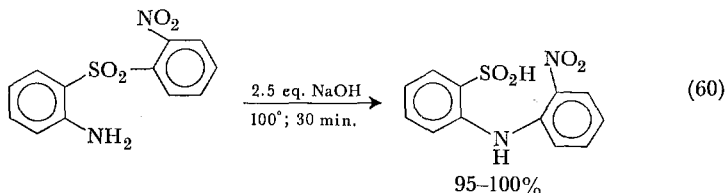
Naturally one can expect that the hydroxyl ion, present in solution competes intermolecularly with the intramolecular action of the phenoxide ion fragment. However, such competitive hydrolytic cleavage can be largely suppressed ( $<5\%$ ) in a medium of aqueous dioxan, which lowers the nucleophilic reactivity of hydroxide ion<sup>55</sup>. The yields of the ordinary rearranged product under such conditions often exceeds 90%.

A similar reaction is found with the nitro group in para-position, and in fact there are few Smiles reactions with other electron attracting groups than the nitro group. On the other hand  $X$  and  $Y$  have been varied widely. Bunnett<sup>1</sup> has reviewed the subject and indicated that the 'leaving' group  $X$  may be  $SO_2$ ,  $SO$ ,  $S$  or  $O$ , and the attacking group  $YH$  may be  $OH$ ,  $SH$  and  $NH_2$  (or a substituted amino group (cf. also reference 549)). The rearrangement is accompanied by striking colour-changes from deep-red to pale-yellow. It is likely that Meisenheimer-type intermediates like **8** are (partly) responsible for this effect.

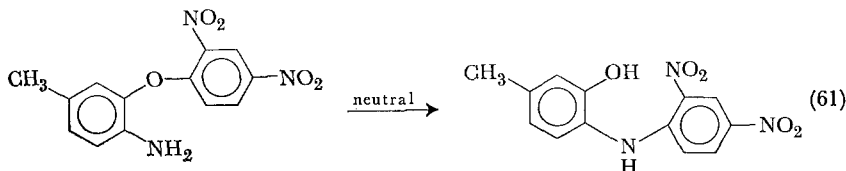
When the nucleophilic activities of  $X^-$  and  $Y^\ominus$  are comparable, the rearrangement becomes reversible. For instance the sulphinic acid with methyl groups at positions 5 and 6<sup>550</sup> is converted back into

a phenol in weakly acidic medium ( $pH = 5$ ) at which the sulphino but not the hydroxyl groups are ionized. In alkaline medium the 'normal' Smiles rearrangement prevails. In buffers with intermediate  $pH$ -values both components are in equilibrium and the composition of the mixture is determined by the  $pH$  of the medium.

Most Smiles rearrangements require alkali in order to convert the group  $YH$  into the more nucleophilic  $Y^-$ . This does not only apply to aromatic hydroxyl groups but also to amino groups because the nucleophilic properties of the undissociated amino group are very weak when a strong electron-attracting neighboring group  $X$  (e.g.  $SO_2$ ) is present (equation 60).

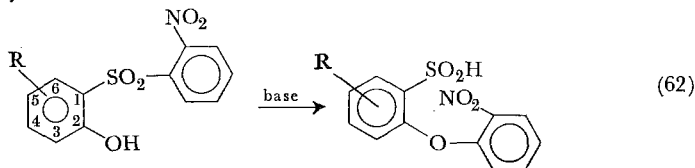


However, when  $X$  is less electron-attracting (e.g.  $X = O$ ) as in diarylethers, rearrangement can be effected by the free amino group without activation by alkali<sup>551</sup> (equation 61).



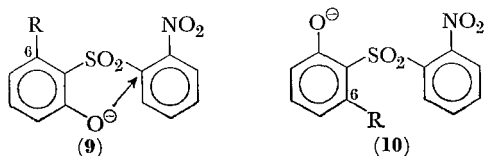
As expected, the presence of a second nitro group promotes rearrangement.

Far more dramatic substituent effects on rates have been noted by Bunnett<sup>64</sup> in the rearrangement of certain diaryl sulphones<sup>552</sup> (equation 62).



Substituents  $R$  (methyl, chlorine or bromine) in the 6-position accelerate the rearrangement a million-fold as compared with the rearrangement rates of the isomeric 4-substituted sulphones. Since electronic effects are roughly equivalent in these positions, the

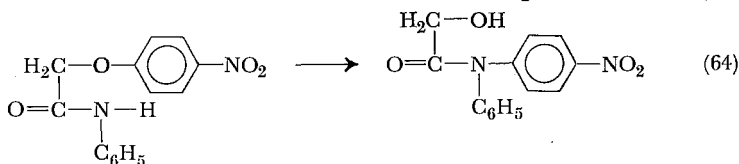
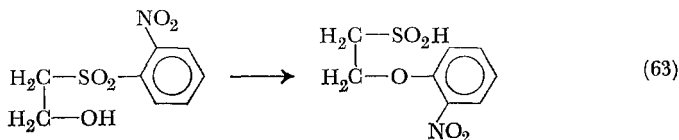
effect is likely to be steric. The enormous effect can be understood by a consideration of rotational conformation **9** and **10**.



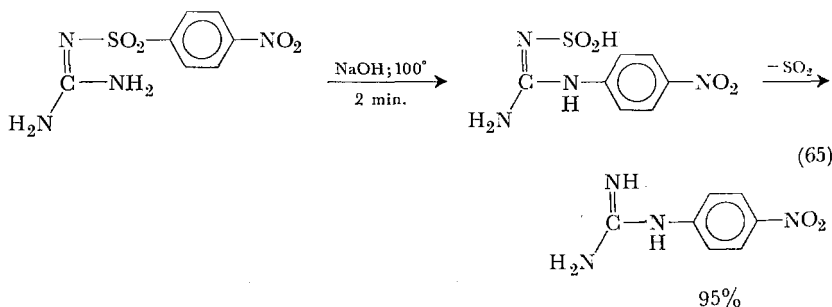
Limiting conformation **9** is prerequisite to rearrangement because it brings the O<sup>-</sup>-group at a minimum distance of the carbon atom which must be attacked.

In conformation **10** this distance is larger and the O<sup>-</sup>-group remains idle. Steric interaction between R and the nitrated ring will raise the energy of this latter conformation and thus favor the relative population of conformation **9**, the more so when R becomes bulkier. Consequently rearrangement occurs faster when hydrogen in the 6-position is replaced by (any) other groups.

As noted earlier, the bridge between the 'leaving' group X and the attacking group Y<sup>-</sup> is not necessarily part of an aromatic ring but can also be aliphatic as exemplified in equations 63–64<sup>553–555</sup>.

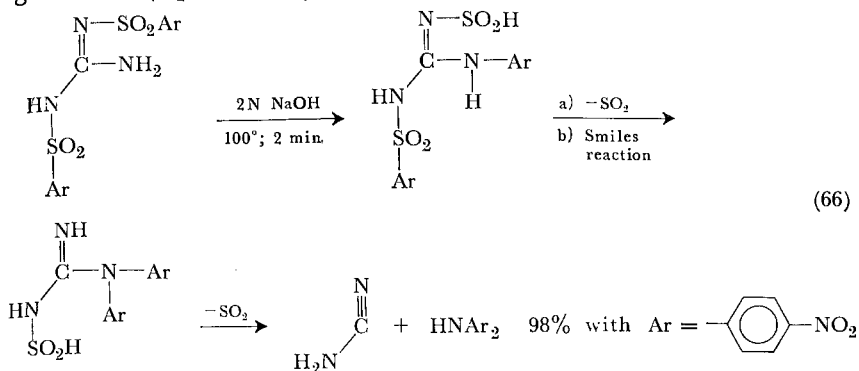


An interesting variation on this theme with a C–N bridge instead of a C–C bridge was found by Backer<sup>556, 557</sup> in the smooth alkaline fission of nitrobenzenesulphonyl guanidines (equation 65).



The final product in its tautomeric form is seen to arise formally by expulsion of  $\text{SO}_2$  from the starting material.

A nearly quantitative double Smiles rearrangement takes place when *two* *p*-nitrobenzenesulphonyl groups (Ar) are present in guanidine (equation 66).

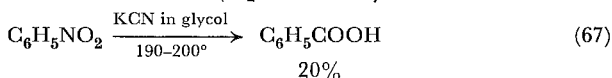


Because the starting material is easily obtained from a sulphonyl chloride and guanidine this has been claimed as a convenient route to nitrated diphenylamines of high purity. The corresponding urea derivatives undergo similar rearrangements, but yields are less favorable.

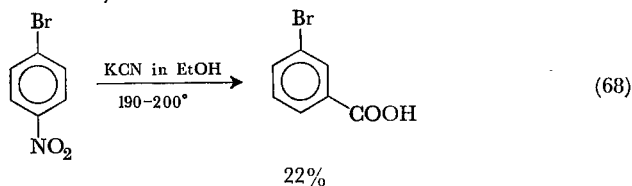
Smiles rearrangements also occur in heterocyclic systems<sup>558</sup>.

## 2. The von Richter reaction

The von Richter reaction involves the removal of an aromatic nitro group by heating with alcoholic potassium cyanide and the introduction of a carboxyl group as shown most simply in the conversion of nitrobenzene into benzoic acid<sup>52</sup> (equation 67).



More revealing is the earliest example described in 1871 by von Richter<sup>559,560</sup> with halogen substituted nitrobenzenes. Surprisingly *p*-bromonitrobenzene yields *m*-bromobenzoic acid and it is equally surprising that there is little nucleophilic halogen displacement by cyanide ion (equation 68).





Similar conversions are possible with chloro- and iodonitrobenzenes and in all cases it has been found that the carboxyl group occupies a position *ortho* to the position originally taken by the nitro group. Accordingly from *m*-bromonitrobenzene a mixture of *o*- and *p*-bromobenzoic acids is obtained<sup>52,559,560</sup>.

Von Richter reactions with similar displacements in other nitroaromatics include some dibromonitrobenzenes<sup>52</sup>, nitroanisoles<sup>52</sup>, *m*-nitrobenzenesulfonic acid<sup>52,561</sup> and 2-nitronaphthalene<sup>562</sup>. Bunnett and coworkers investigated the effect of various substituents<sup>62</sup> and improved reaction conditions<sup>56</sup>. A large excess of potassium cyanide in refluxing 48% aqueous ethanol was found to give an optimum conversion of *p*-chloronitrobenzene into *m*-chlorobenzoic acid (42%).

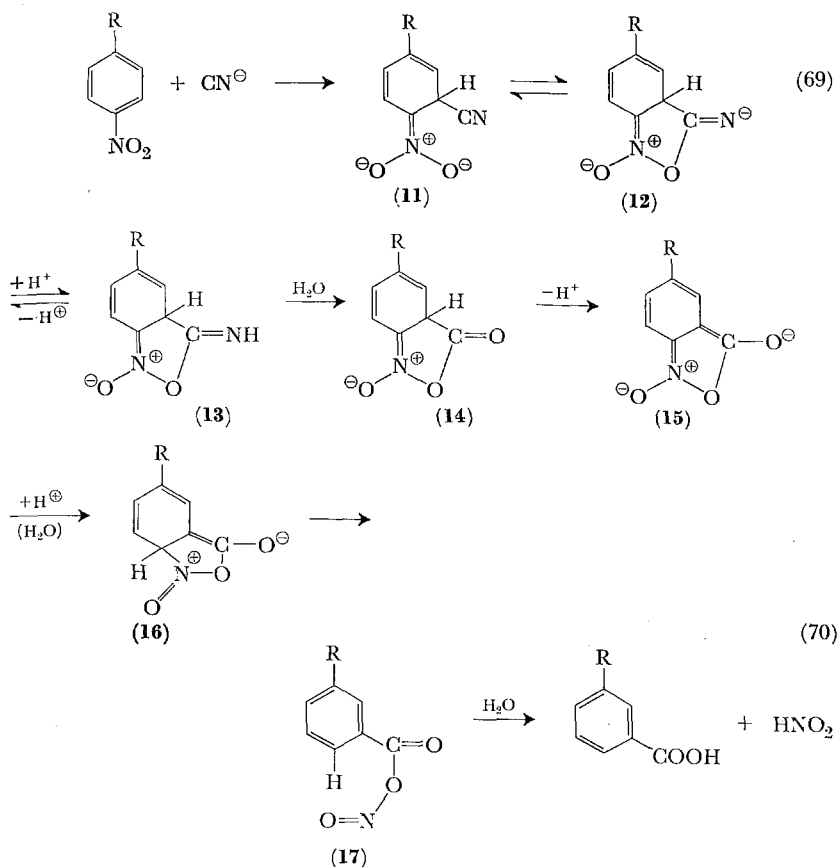
Kinetic studies which played an important role in the establishment of the mechanism of nucleophilic halogen displacement are not feasible for a reaction with such low yields. The complicated mechanism of the von Richter reaction had to be elucidated along other routes a.o. careful product analysis and tracer studies.

The following observations, made by Bunnett<sup>52</sup> and coworkers are significant:

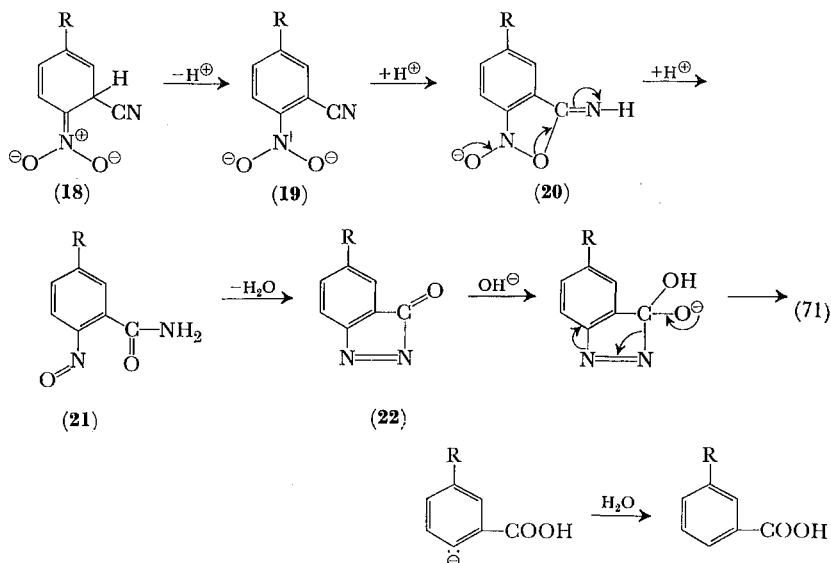
- (a) the carboxyl group appears without exception *ortho* to the position vacated by the nitro group.
- (b) experiments with selectively deuterated compounds show that hydrogen from hydroxylic solvents is incorporated in the aromatic nucleus.
- (c) the benzoic acids obtained are not formed *via* the corresponding nitriles or amides, because these resist hydrolysis under the reaction conditions.
- (d) nitrite ion is a byproduct.

These and other observations led Bunnett to the following interpretation (equations 69–70).

It is seen that the hydrogen introduced at the position vacated by the nitro group is derived from the solvent, **15** → **17**. A further consequence of this mechanism is that one oxygen in the carboxyl group of the final product is derived from the solvent while the other oxygen comes from the original nitro group. This has been substantiated by Samuel<sup>563</sup> in a study of the von Richter reaction in an alcohol-water solvent enriched with <sup>18</sup>O. Although this mechanism explains adequately the formation of some nitrite anion, the Bunnett mechanism does not account satisfactorily for the fate of the two nitrogen atoms from the cyano and nitro group.



Rosenblum<sup>564</sup> reinvestigated the von Richter reaction with *p*-chloronitrobenzene and found that nitrogen gas, hitherto undetected, is liberated in amounts nearly equivalent to the yield of *m*-chlorobenzoic acid. This nitrogen gas cannot be derived from reaction of ammonia (from the hydrolysis of **13**) with nitrite ion (from the hydrolysis of **17**), for when the reaction is carried out in the presence of <sup>15</sup>NH<sub>3</sub>, the nitrogen gas liberated remains unlabeled. Nevertheless one of the two nitrogen atoms in the evolved nitrogen gas must arise from the nitro group as demonstrated by reaction with <sup>15</sup>N-labeled *p*-chloronitrobenzene. The remaining nitrogen must then be derived from the cyanide ion, but *via* a reaction path not involving ammonia. These findings led Rosenblum to the following modification of the Bunnett mechanism (equation 71).



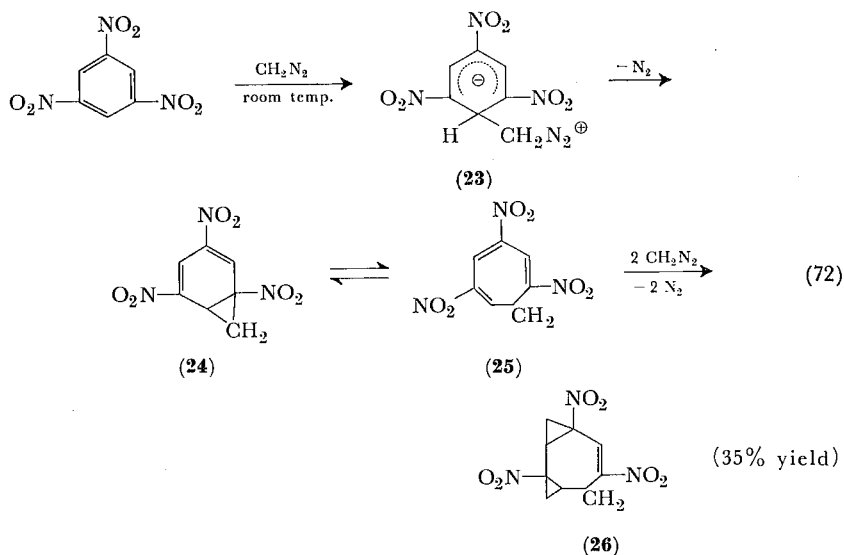
The intermediate dianion **19** is speculative and seems not necessary to explain the formation of the amide **21** as pointed out by L'Ecuyer<sup>565</sup>. The latter might well result from isomerization of the imide **12** proposed by Bunnett. More essential is the new intermediary 3-indazolone **14**. The compound (with  $R = H$ ) has been synthesized by Ullman and Bartkus<sup>566</sup> by low temperature oxidation of a suitable dihydroderivative. When added to a solution of sodium cyanide in aqueous ethanol nitrogen evolution is instantaneous and benzoic acid is obtained in a yield of 80 %. No phenol or phenetole is found among the reaction products, indicating the absence of benzyne type intermediates in accordance with the absence of benzyne-derived products from the von Richter reaction. All these findings are in agreement with the reaction sequence proposed by Rosenblum. They do not rule out the possibility that the Bunnett scheme is valid to some extent, which could account for small amounts of nitrite ion.

That there are still other routes from nitro compounds to carboxylic acids is also apparent from investigations by Cullen and L'Ecuyer<sup>567</sup>. These authors isolated from nitronaphthalenes reduction products with high molecular weight and uncertain structure, but with the property of yielding von Richter type products upon treatment with alcoholic solutions of cyanides. Reduction products

(azo- and azoxy products) have also been found in the benzene series, but these remain unchanged under the conditions of the von Richter reaction and are therefore no intermediates.

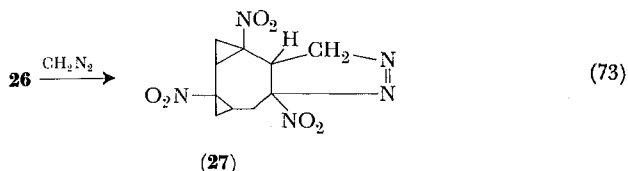
### 3. Ring enlargement of polynitroaromatics

At the turn of the century Heinke<sup>568</sup> and von Pechmann<sup>569</sup> noticed that diazomethane reacts rapidly with 1,3,5-trinitrobenzene and its derivatives with at least one hydrogen at the benzene nucleus e.g. trinitrotoluene, picric chloride, picric acetate and (less easily) trinitroxylylene. Trinitromesitylene does not react and neither do mono- and dinitrobenzene. In the authors laboratory<sup>570-575</sup> it was found that three (and no less) methylene groups can be introduced into 1,3,5-trinitrobenzene (TNB) by reaction with three equivalents of diazomethane. The structure of the stable product **25** has been established by spectroscopy and oxidative degradation. Its formation is explained with the following reaction sequence (equation 72).



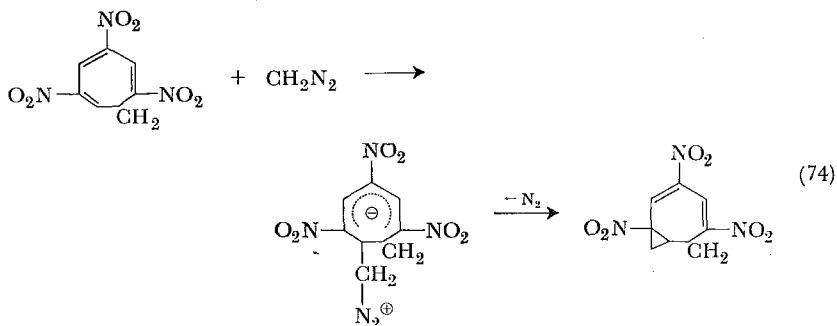
The first step is a nucleophilic addition of diazomethane to trinitrobenzene. The intermediate Meisenheimer type complex **23** has been assumed because on mixing of the reacting components the ethereal solution becomes deep red. Although the colour might also be associated with a charge transfer complex, intermediate **23** is a logical

prerequisite to the norcaradiene **24**. It is well known that this system rearranges easily to a cycloheptatriene<sup>576,577</sup> which in the present case contains three aliphatic nitro olefinic fragments, two of which react so quickly with diazomethane to form cyclopropane rings, that all attempts to isolate **25** have failed. With molar ratios  $\text{TNB}/\text{CH}_2\text{N}_2 = 1:1$  or  $1:2$ , only **26** is found together with unchanged TNB. With a large excess of diazomethane (e.g. molar ratio  $1:4$ ) the double bond in **26** is also attacked, but this does not introduce a third cyclopropane ring: it leads—probably by 1,3-dipolar addition<sup>578–581</sup>—to a stable pyrazoline **27**, which has the same properties as the product isolated exclusively in earlier investigations<sup>568,569</sup> (equation 73).



The various reactivities of the double bonds in the intermediary cycloheptatriene derivative **25** have been the subject of theoretical calculations<sup>582</sup>.

Charge delocalization in intermediate adducts seems to favor loss of nitrogen and consequently cyclopropane-formation e.g. in the addition of the second molecule of diazomethane (equation 74).



On the other hand if charge delocalization is less effective—as in the attack of isolated nitro olefinic bonds—the betainic intermediate is probably not formed at all and 1,3-dipolar attack of diazomethane leads directly to a pyrazoline. This is confirmed by the types of product obtained from diazomethane with picric acid<sup>583,584</sup>.

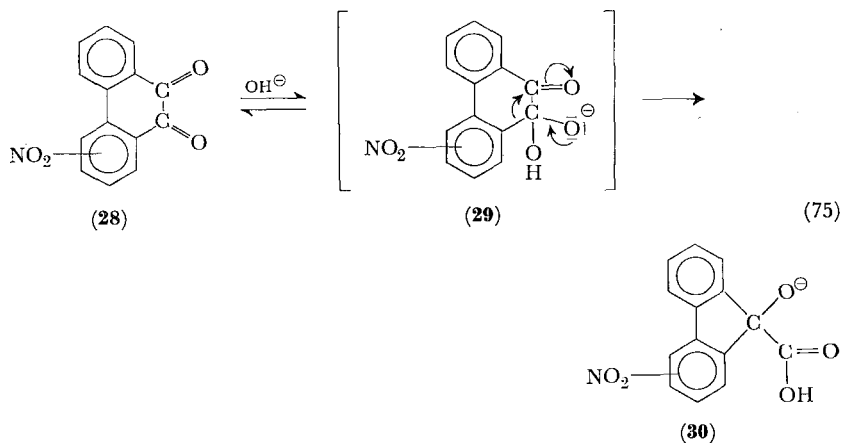
Phenyldiazomethane gives similar reaction products with *sym*.

trinitrobenzene as diazomethane. With more reactive diazoalkanes such as diazoethane and diazopropane ('dimethyldiazomethane') derivatives are obtained not only from cycloheptatriene but also from norcaradiene<sup>585</sup>. Apparently the more reactive diazoalkanes attack the norcaradiene in competition with its isomerization to a cycloheptatriene. The complicated reaction mixtures consist mostly of pyrazolines.

### Other rearrangements

Many reactions that proceed via carbanions (in or before rate determining steps) are strongly promoted by nitro groups in the substrate. A striking example is the benzilic rearrangement of some nitrophenanthra-9,10-quinones.

Like benzil these diketones rearrange to salts of  $\alpha$ -hydroxy acids. In the absence of nitro groups, strong alkali and elevated temperature are required. However, nitrophenanthrene-9,10-quinones react under far less drastic conditions with dilute bases at room temperature<sup>586</sup> (equation 75).



Proton transfer within the ion **30** gives the salt of an  $\alpha$ -hydroxy acid. If the quinone system is taken as part of the whole aromatic phenanthrene structure, this type of reaction must be considered as a nucleophilic aromatic rearrangement. The nitro groups render the carbonyl groups highly susceptible to nucleophilic attack by hydroxyl ion.

The negative charge in the (hypothetical) intermediate anion **29** is largely localized on oxygen by lack of mesomeric interaction with

the nitro groups, and this promotes the rearrangement. This effect is apparently more important than the (usually low) migratory aptitude of a nitro-aromatic fragment towards a carbonium-type center i.e. of the carbonyl group in **29**.

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## CHAPTER 9

# Methods of formation of the nitramino group, its properties and reactions

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I. INTRODUCTION . . . . .	614
II. PRIMARY NITRAMINES . . . . .	614
III. PRIMARY ISONITRAMINES . . . . .	619
IV. PRIMARY NITRAMIDES . . . . .	624
V. SECONDARY NITRAMINES . . . . .	628
VI. SECONDARY ISONITRAMINES . . . . .	637
VII. SECONDARY NITRAMIDES . . . . .	639
VIII. NITRIMINES . . . . .	645
IX. POLYNITRIMINES . . . . .	649
A. Polynitrimines from Nitric Acid . . . . .	651
B. Polynitrimines from Acetic Anhydride and Nitrates . . . . .	660
X. PHYSICAL PROPERTIES OF NITRAMINES . . . . .	670
A. Vibrational Spectra . . . . .	670
B. Ultraviolet Spectra . . . . .	673
C. X-Ray Diffraction . . . . .	674
D. Nuclear Magnetic Resonance Spectra . . . . .	674
E. Electrical Polarization . . . . .	675
XI. REFERENCES . . . . .	680

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## I. INTRODUCTION

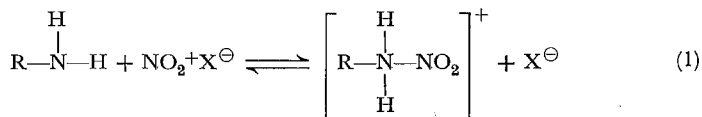
Except in time of war when nitramines are exploited as explosives because of their high and rapid energy release they have been of little chemical interest in recent years. For this reason it is surprising to some that nitramines rate a separate functional-group classification in Beilstein's Handbuch. Historical investigation shows that this prominence was deserved from 1885 until 1920.

The first nitramino compounds were made by Peter Griess<sup>1</sup> but the structure of this functional group was first made known by von Romburgh<sup>2</sup> from his investigations of a substance made by Mertens<sup>3</sup> by nitration of dimethylaniline. This substance is *N*-picryl-*N*-methylnitramine (TETRYL). Franchimont, who encouraged von Romburgh to continue the study of aromatic nitramines, investigated alkyl and acyl nitramines<sup>4</sup> and first isolated a primary nitramine. Great interest centered on the acidic properties of these  $\text{RNHNO}_2$  compounds especially by Bamberger<sup>5</sup>, Hinsberg<sup>6</sup> and Hantzsch<sup>7</sup>.

The parent nitramine,  $\text{NO}_2\text{NH}_2$ , was isolated by Thiele and Lachman<sup>8</sup> and named nitramide, probably by analogy with chloramide. This name caused some confusion in nomenclature which was mentioned in Backer's valuable, though now outdated review<sup>9</sup> and which has not yet been properly resolved. For purposes of this chapter the substance will be called 'nitramine' and its substitution derivatives will be named as nitramines or nitramino compounds. When the nitramino group is bonded to the carbon of a carbonyl group it becomes a nitramide. When the nitramino group is coupled by loss of water with a carbonyl it becomes a nitrimine. Variations of these three categories are listed as isonitramines, isonitramides and polynitrimines. These eight categories are exemplified as shown at the top of page 615.

## II. PRIMARY NITRAMINES

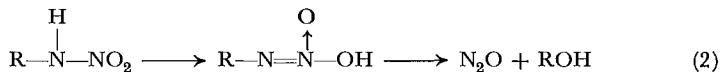
With a few exceptions involving aromatic amines<sup>10-16</sup> where the initial nitramine becomes the amino-nitro derivative by rearrangement or cross nitration) most primary amines cannot be nitrated directly by nitric acid. This seems to be due both to the relative instability of the monosubstituted nitrammonium ion (equation 1)



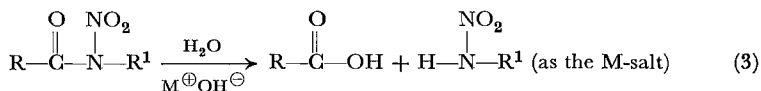
Type	Example	Formula
1. primary nitramine	methylnitramine	$\text{CH}_3-\overset{\text{H}}{\underset{ }{\text{N}}}-\text{NO}_2$
2. primary isonitramine	tautomer of 1	$\text{CH}_3-\text{N}=\overset{\text{O}}{\underset{\uparrow}{\text{N}}}-\text{OH}$
3. primary nitramide	nitrourethane	$\text{C}_2\text{H}_5-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\overset{\text{H}}{\underset{ }{\text{N}}}-\text{NO}_2$
4. secondary nitramine	dimethylnitramine	$\text{CH}_3-\overset{\text{NO}_2}{\underset{ }{\text{N}}}-\text{CH}_3$
5. secondary isonitramine	methyl methylisonitramine	$\text{CH}_3-\text{O}-\overset{\text{O}}{\underset{\uparrow}{\text{N}}}=\text{N}-\text{CH}_3$
6. secondary nitramide	methylnitrourea	$\text{CH}_3-\overset{\text{NO}_2}{\underset{ }{\text{N}}}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}_2$
7. nitrimine	furfuralnitrimine	$\text{C}_4\text{H}_4\text{O}-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{N}-\text{NO}_2$
8. polynitrimine	cyclonite	$(\text{CH}_2=\text{NNO}_2)_3$

Each one of this classification will be discussed in turn.

and to the instability of the tautomeric isonitramine in acid (equation 2).



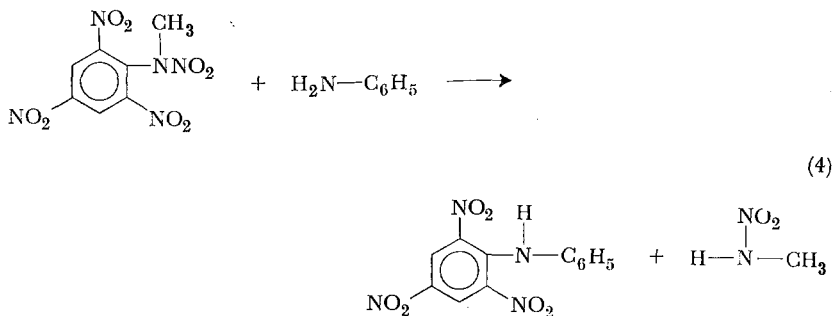
The earliest method of preparation, that of Franchimont and Klobbie<sup>4</sup>, involved the alkaline (better ammoniacal) hydrolysis of nitramides (equation 3); indeed this was the method by which Thiele and Lachman<sup>8</sup> obtained the parent, nitramine (so-called nitramide), and it enabled the preparation of methylnitramine and



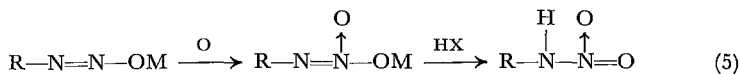
many others of this homologous series. Obviously the reaction is dependent upon charge distribution. For this reason it is not surprising that the reaction applies also to the decompositions of some aromatic-aliphatic secondary nitramines<sup>17</sup> with ammonia or amines



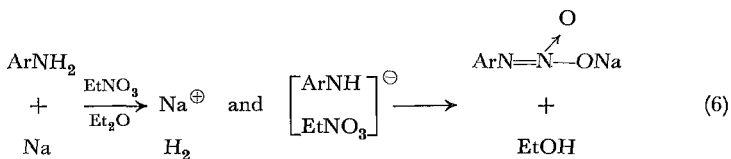
(equation 4).



The classical method by which Bamberger<sup>5</sup>, Hinsberg<sup>6</sup> and later Thiele<sup>11</sup> formed primary nitramines involves oxidation of salts of diazotates by means of hypochlorite<sup>12</sup>, permanganate or (better) potassium ferricyanide (equation 5).



By contrast to electrophilic reactions in which a nitronium ion or some modification of it is involved, is the nucleophilic reaction of Angeli<sup>13</sup> in which a complex anion from ethyl nitrate and the deprotonated amine probably is involved (equation 6).

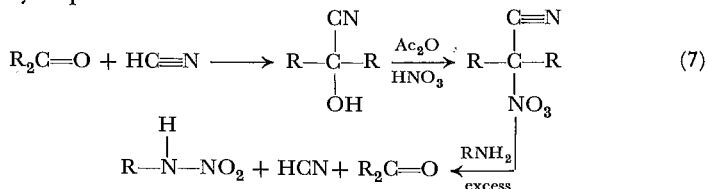


Later the reaction was altered by Bamberger<sup>14</sup> by use of potassium ethoxide instead of the metal. In a further modification the alkali metal salt of the amine has been formed by use of butyl lithium<sup>15</sup> prior to addition of ethyl nitrate.

This reaction of Angeli is useful not only in the preparation of alkyl primary nitramines but also in order to prepare aromatic primary nitramines<sup>16</sup> (as the metal isonitraminate) which are prone to undergo the Orton rearrangement in acidic media.

Perhaps the most important modification of the Angeli reaction has been effected by use of other than simple primary alkyl nitrates. In fact the revival of the Angeli reaction was brought about by Emmons and Freeman<sup>17</sup>. They used cyanohydrin nitrates from

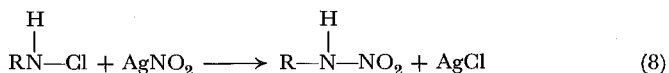
acetone or cyclopentanone



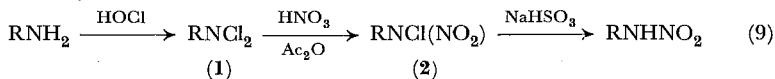
and first elucidated the reaction presented in equation (7). Their method is wasteful since the base in their systems is derived from an excess of the amine. It may be expected that their reaction will be improved by use of metal salts.

Although nitrogen pentoxide is commonly considered as a source of nitronium ion it is probable that its reaction in ether or carbon tetrachloride, like that of nitryl chloride<sup>18</sup>, is similar to the Emmons-Freeman modification of the Angeli reaction. The poor yields would seem to be due to insufficient excess of amine. Undoubtedly the better yields when nitryl fluoride is added to ammonia or a primary amine<sup>19</sup> are due to the excess of the latter substances throughout most of the reaction.

A relatively unimportant method for low-yield preparation of primary nitramines has been reported by Berg<sup>20</sup> (equation 8).



The low yield would be expected in view of the instability of monochloramines. On the other hand dichloramines **1** have been found to be nitratable to give good yields of organo-chloronitramines **2**. These compounds are readily reduced to the primary nitramines by use of sodium bisulfite. This series of reactions thus provides a relatively recent method for synthesis of primary nitramines<sup>21</sup> (equation 9).

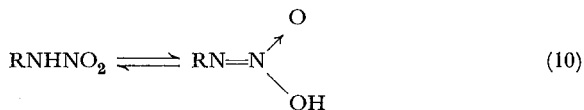


The reaction, which is of general applicability with aliphatic amines gives high yields with normal alkyl amines. The yields are less satisfactory from secondary alkyl amines because of a side-reaction which forms a nitrimine by loss of hydrogen chloride.

In respect of physical properties the primary nitramines convey some characteristics of the nitro group. The substances are liquids or low-melting solids. The nitramino group, as such, absorbs strongly

at 225–240 m $\mu$ .  $E_{\max}$  is about 7000 for primary nitramines by contrast to about 5500 for secondary nitramines. The nitramino group is transparent in the visible region, but it absorbs characteristically at about 6.6, 7.8, 8.9 and 13.2 microns. In common with *C*-nitro and *O*-nitro the *N*-nitro group increases the density of substances in which it exists as a substituent. For example compare 1,2-diaminoethane ( $d_4^{20}$  0.914) with 1,2-dinitraminoethane ( $d_{23}^{23}$  1.696) to which the amine can be converted<sup>21</sup>. The explosibility of the lower nitramines are due to high energy release and high density; these substances should be handled with caution.

The most significant chemical property of the primary nitramines is acidity. They are weaker than the corresponding carboxylic acids but they differ from the latter because the dissociation constants of the primary nitramines are strongly temperature-dependent. Hantzsch<sup>22</sup> found that the dissociation constant of methylnitramine changed from  $0.30 \times 10^{-5}$  at 0° to  $0.72 \times 10^{-5}$  at 25° and  $0.86 \times 10^{-5}$  at 35°. The same behavior was observed by Euler<sup>23</sup> for phenylnitramine. His results have been combined with that of Hantzsch<sup>24</sup> to show that this stronger acid changes from  $12.4 \times 10^{-5}$  at 0° to  $13.4 \times 10^{-5}$  at 10°,  $18 \times 10^{-5}$  at 20°, and  $23 \times 10^{-5}$  at 25°. Hantzsch considers this behavior as partial evidence for pseudo-acid equilibria. The pseudo form is thought to be the nitramine and the aciform that of the isonitramine (equation 10).



The salts of primary nitramines have been presumed to involve the aci (isonitramine) form. On the basis of this assumption a comparison has been made between the X-ray diffraction analysis of 1,2-dinitraminoethane<sup>25</sup> and that of its disodium salt<sup>26</sup>. A comparison of bond lengths and angles found for the dinitramine (bracketted) and its sodium salt (unbracketted) are shown in Figure 1.

It may be seen that although the two nitrogen–oxygen bonds are longer in the disodium salt than in the nitramine they are, surprisingly, equal in length. Many of the bond angles are different and this is no doubt due to the difference in the nitrogen–nitrogen bond lengths in the acid and its sodium salt. Perhaps more significant is the fact that in the salt the sodium atom is closer to oxygen than to nitrogen. However, the difference is not sufficiently great to

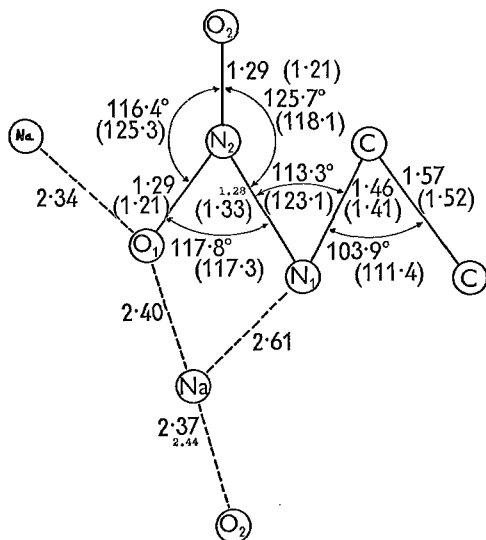
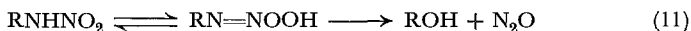


FIGURE 1. X-ray diffraction analysis of 1,2-dinitroaminoethane and its sodium salt.

justify the separate structural designations of nitramine and isonitramine\*. Of course it must be realized that the organization in the crystal has no direct relationship to the circumstance in solution. X-ray diffraction studies contribute much to a knowledge of chemicals but very little to a knowledge of chemical reaction.

### III. PRIMARY ISONITRAMINES

The possibility of an equilibrium between a primary nitramine,  $\text{RNHNO}_2$ , and the tautomer called the isonitramine,  $\text{RN}=\text{NOOH}$ , has been considered throughout the history of nitramines. Franchimont believed that acids displace the equilibrium in favor of the isonitramine especially with increasing temperature; he could explain in this way the instability of primary nitramines toward mineral acid (equation 11).

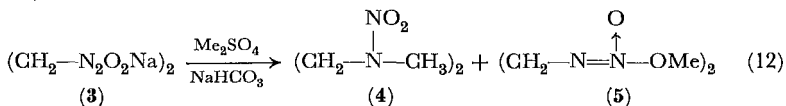


solution, but he had no real proof for this postulation. However, a proof that one nitramine exists in two isomeric forms has been demonstrated by Orton<sup>27</sup>. He acidified an alkaline solution of 2,4-dibromo-6-nitrophenylnitramine. The original precipitate, presumably the isonitramine, is colorless but it soon turns into the yellow nitramine.

The identity of the nitramine-isonitramine system has also been sought by reaction with diazomethane, a reagent that is said to react more readily with the hydroxyl than with the imino group. However, the meagre results have been in question<sup>28,29</sup> since methylnitramine gives exclusively *N*-methylation while phenylnitramine affords only some *N*-methylation and principally *O*-methylation. It is of interest that no one has seriously questioned the structure of phenylnitramine as a unique species.

A different aromatic nitramine, 2-nitraminothiazole, with diazomethane gives a quantitative yield of *N*-methylated product. On the other hand in alkaline solution this reactant, 2-nitraminothiazole<sup>30</sup> may have formed some of the secondary isonitramine when the sodium salt (readily formed by treatment with aqueous sodium bicarbonate) was treated with dimethyl sulfate, because the product, *N*-methylnitraminothiazole was obtained in lower yield (85%) and purity than is observed with diazomethane. It may be assumed that there is attack at nitrogen and at oxygen in the 'nitraminate' ion.

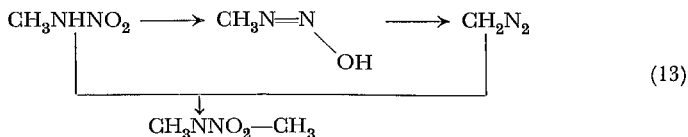
Although there is little doubt about the primary nitramine-isonitramine tautomerism it is doubtful that Hantzsch's pseudo-acidity is applicable. In alkaline solution the reacting species is probably the anion which, as a resonance hybrid, is neither of the tautomers although it will react, say with dimethyl sulfate, to give derivatives of both. For example, the products from 1,2-dinitraminoethane<sup>26</sup> (as its sodium salt **3**) are compounds **4** and **5** (equation 12).



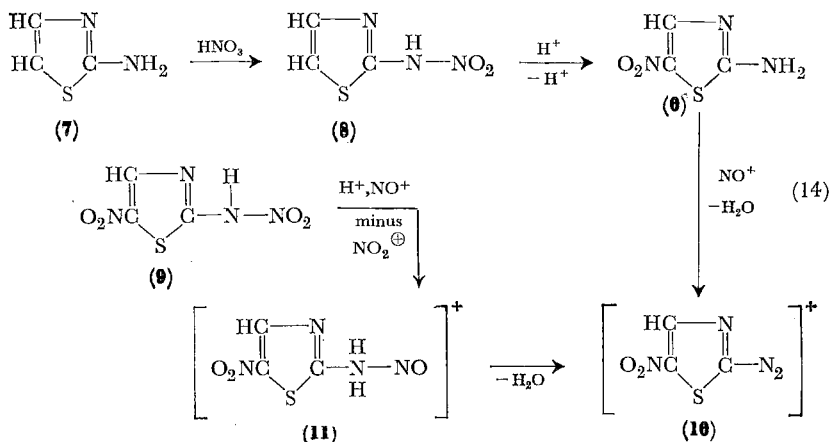
The product ratio, three of **4** to one of **5** cannot of course be presumptive of nitramine-isonitramine ratio because the 'nitraminate' ion is involved.

An unexpected reaction of primary nitramine occurs with nitrous acid; diazotization occurs. The reaction suggests initial hydration of

the nitramine to give the analogous organo-ammonium nitrate which subsequently is diazotized. When methylnitramine is treated with nitrous acid the expected product, methanol, is obtained together with dimethylnitramine and the isomeric isonitramine<sup>31</sup>. These byproducts indicate the transient existence of methyldiazotic acid and its dehydration product, diazomethane, which presumably reacts with the original nitramine and its isomer (equation 13).



Because of the relative stability of aromatic diazonium salts they are the principal, oftentimes quantitative, products from treatment of substances like phenylnitramine<sup>32</sup> with nitrous acid. Sometimes it is more convenient to obtain the diazonium salt from the primary nitramine than from the amine. For example 5-nitro-2-aminothiazole (6) may be obtained by nitration of 2-aminothiazole (7) but the product is likely to be contaminated with 2-nitroaminothiazole (8) which is involved in an intermediate step<sup>30</sup> \*. On the other hand 2-nitramino-5-nitrothiazole (9) is prepared easily and in good yield of high purity. Consequently it is advantageous to obtain 5-nitrothiazole diazonium salt (10) by treatment of the nitramine 9 rather than of the amine with nitrous acid (equation 14).



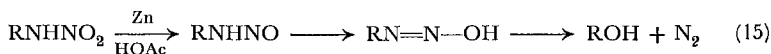
\* This nitramine is wrongly specified as 2-amino-5-nitrothiazole in the experimental part of this report.

Although the conversion of **9** to **10** has been referred to as a diazotization or a reduction, it would seem more reasonable to consider it as an intra-ion exchange between 5-nitrothiazolyl-ammononitronium ion (**9** plus a proton) and 5-nitrothiazoyl-ammonitrosonium ion, **11**. This interpretation is supported by evidence that the ostensible rearrangement of **8** to **6** is not intramolecular but, instead, is a bimolecular interchange of ammono-coöordinated nitronium ion (**8** plus a proton) to sextet-coöordinated nitronium ion (**6** plus a proton)<sup>33</sup>.

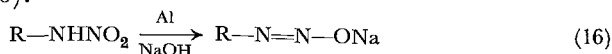
The reaction of **9** with nitrous acid precludes the alternative isomers  $\Delta^4$ -thiazoliny-2-nitrimine because, as will be shown later, nitrimines do not undergo this reaction. However, a better and very useful criterion for the presence of a nitramine group is the Franchimont test. Although Franchimont originally proposed this test for secondary nitramines and nitramides<sup>31</sup> it is useful as well for primary nitramines and nitramides. The candidate substance is dissolved in acetic acid to which is added one of many aromatic amines; the best is dimethylaniline. Subsequently a 'messerspitze' of zinc dust is added; too much is deleterious. The appearance of a green color, with dimethylaniline, is presumptive for a nitramine.

As might be expected, primary nitramines are stable toward non-acidic oxidizing agents, but they are easily reduced. However, the product is seldom the hydrazine in good yield. Instead the overall reaction is that of scission at the nitrogen-nitrogen bond. For example, methylnitramine is converted by zinc in acetic acid to methanol. Alkaline reduction with sodium amalgam gives methylamine<sup>34</sup>. Reduction with aluminum in alkaline solution was the classical method<sup>18</sup> whereby Thiele obtained the salt of methylisodiazotate. Finally methylhydrazine is obtained in very low yield when methylnitramine is treated with zinc in hydrochloric acid<sup>35</sup>. However, reduction of aromatic primary nitramines are somewhat more favorable. Phenylnitramine is converted to benzenediazotic acid by zinc and acetic acid<sup>32,36-38</sup>, but sodium amalgam converts it to phenylhydrazine. In both instances there is some fission at the nitrogen-nitrogen bond.

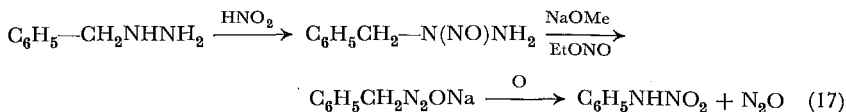
The reduction of primary nitramines to hydrazines is a very unsatisfactory reaction. This is probably because the intermediate nitrosamine decomposes<sup>34</sup> (equation 15).



But a few percent of hydrazines are sometimes obtained when zinc and hydrochloric acid are used<sup>35</sup>. Hydrogenolysis occurs at the nitrogen–nitrogen bond when sodium amalgam is used<sup>18</sup> but aluminum in alkaline solution gives the salt of methyldiazotic acid<sup>39</sup> (equation 16).

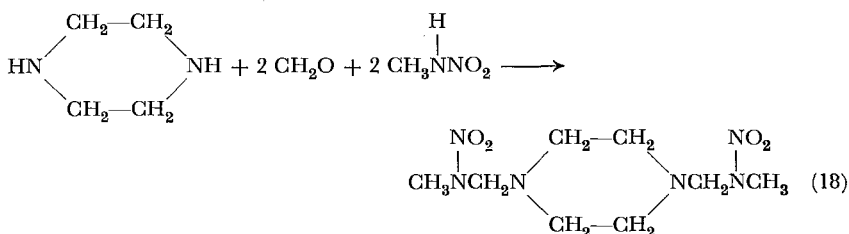


The reaction is of the reverse of Thiele's preparation of alkyl-nitramines by ferricyanide oxidation of the alkyl-diazotic acid salts, which he made by nitrosation of alkylhydrazines<sup>39</sup> (equation 17).

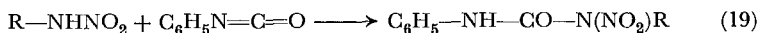


In some instances such as the reduction of nitrohydantoin none of the hydrazine is obtained and only hydrantoin itself is the product<sup>40</sup>. This nitrogen–nitrogen fission occurs to some degree with all true nitramines and nitramides. In fact hydrazines are obtained better from nitrosamines or nitrosamides when they are available than from the nitro analogues.

Franchimont seems to have effected a Mannich-type reaction almost twenty years<sup>41, 42</sup> before Mannich discovered this method of synthesis. Typical is the reaction of methylnitramine with piperazine and formaldehyde. Like the Mannich reaction it is reversible in presence of alkali (equation 18).



As might be expected from the labile hydrogen on aliphatic primary nitramines reaction occurs with isocyanates with formation of substituted nitroureas<sup>43</sup> (equation 19). Evidence that phenyl-

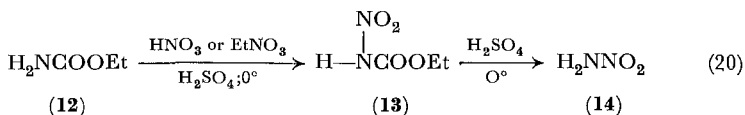


nitramine and nitramine itself tend toward the isonitramine structure,  $\text{RN=N(O)OH}$ , is supported by the fact that these substances do not form ureas with isocyanates<sup>37</sup>.

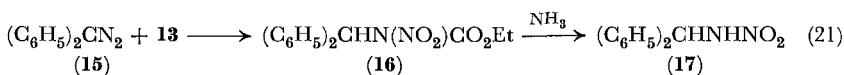


#### IV. PRIMARY NITRAMIDES

Although amides were the first compounds to be nitrated<sup>44</sup> the reaction is a difficult one involving careful regulation of nitric acid or its esters. Perhaps the best example is found in the excellent work of Thiele<sup>45</sup> when he nitrated urethane (**12**) as an intermediate in the subsequent preparation of nitramine itself (equation 20).

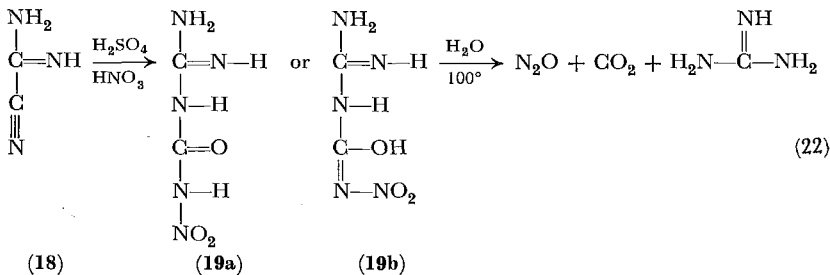


The nitrourethane **13** has been used for the preparation of more complex nitramides (such as **16**) which are then sources of the analogous nitramines **17**<sup>46</sup>. These syntheses are based on the clean reaction of diazomethanes (such as **15**) with nitrourethane (equation 21).

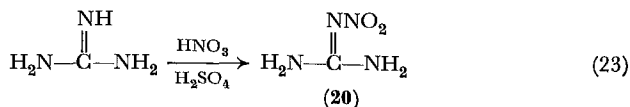


During twenty years after Franchimont's original work, a large number of linear and cyclic amides were nitrated either as sources, by hydrolysis, of primary nitramines or else as sources of hydrazines by reduction<sup>9</sup>. However, the reduction is frequently unsatisfactory, although it works well for conversion of nitroguanidine to amino-guanidine<sup>47</sup> and nitrosoguanidine.

Besides urethane, Thiele nitrated urea<sup>45</sup> by treatment of urea nitrate with sulfuric acid. Also he nitrated biuret<sup>48</sup> (to mono or dinitrobiuret) and obtained nitrodicyandiamidine<sup>49</sup> (guanylnitro-urea, **19**) from dicyandiamide (**18**) (equation 22). It may also be prepared from dicyandiamidine (guanylurea), the hydrolysis product of **18**. Nitrodicyandiamidine (**19**) is of interest from several



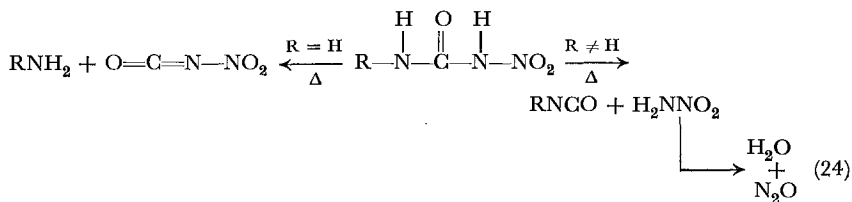
aspects. First, Thiele demonstrated by hydrolysis to guanidine that the nitro group is attached to the urea-like part of the molecule. However, it is probable that the structure **19a** which Thiele assigned is incorrect. Thiele also nitrated guanidine and was at first undecided about the structure<sup>50</sup> but he finally called it a primary nitramide as he did **19a**. Subsequently<sup>51</sup> it has been shown that nitroguanidine has the nitrimide structure **20** (equation 23). Since nitrodicyandia-



midine shows similar characteristics it is probably **19b**. It does not give the Franchimont test characteristic of nitramides like nitrourea and nitrobiuret nor does it react with diazomethane as do these substances. Added to these observations by the author is the fact that it is neutral like nitroguanidine when it is first treated with aqueous alkali.

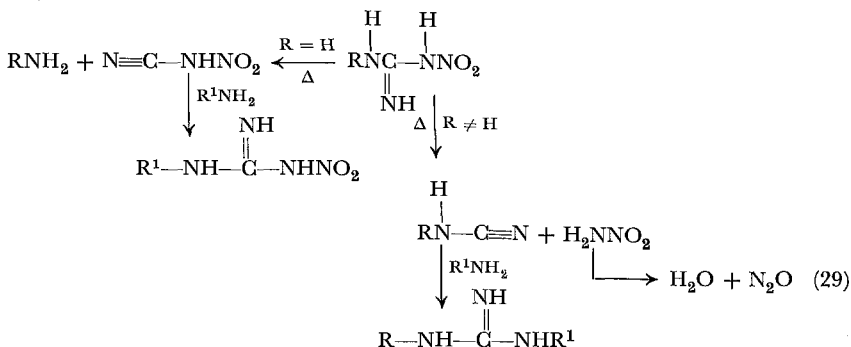
It must be stressed that no generalization can be drawn in respect of the nitrimide versus nitramide structure. For example the properties described for dinitrobiguanidine indicate that it is at least partly an ammononitramide<sup>52</sup>.

The chemistry of nitrourea, nitroguanidine and their alkyl derivatives have been studied extensively by T. L. Davis and his co-workers. Davis<sup>53</sup> devised the term 'dearrangement' to explain the decomposition of nitrourea although he did not isolate any of the primary products of this decomposition (equation 24).



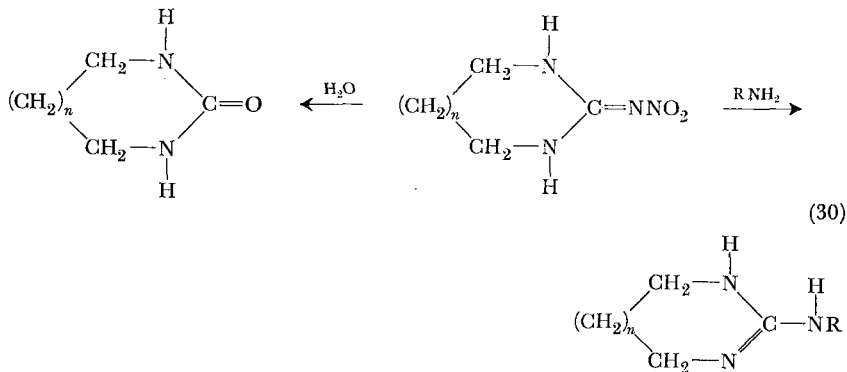
Naturally nitramine was already known to be unstable under the conditions of thermal decomposition but nitroisocyanate was and still is unknown. The 'dearrangement', however hypothetical, did explain the reactions that actually occurred. For example the reaction of nitrourea with equivalent amounts of amines may be depicted from nitroisocyanate in order to account for the products, *N*-alkyl or aryl-*N'*-nitroureas that are obtained (equation 25). But these products also will react with more of the amines. Since the nitro





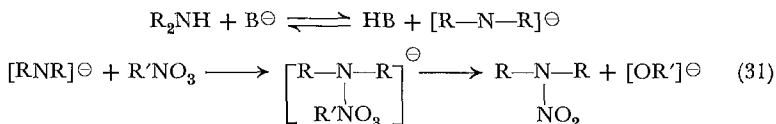
type of product (equation 29). The latter compound has since been isolated in salt form by another method<sup>55</sup>. As is the case with the ureas, with nitroguanidine the principal product upon treatment with an alkyl or aryl amine is the 3-alkyl or aryl-substituted nitroguanidine, whereas a 3-alkyl or aryl-substituted nitroguanidine reacts, with ostensible loss of the nitro group, to give a 1,3-disubstituted guanidine. Of course these are the main products that are obtained from the two reactions but there is a discrepancy: Davis assumed the wrong structure for nitroguanidine as  $\text{H}_2\text{N}(\text{C}=\text{NH})\text{NHNO}_2$ . In order to conform with Davis' concepts of 'de-arrangement' one must assume that nitroguanidine in its isolated form,  $(\text{NH}_2)\text{C}=\text{NNO}_2$ , rearranges to the aci-form that Davis thought to be the structure. Such an isomerization in the presence of basic amines is not unreasonable, but it allows for a number of alternative mechanisms. It is doubtful today whether Davis' concept of 'dearrangement' is very useful.

The replacement of the nitro group by the amino group has been extended to cyclic nitroguanidines<sup>56</sup> but the water used in the reaction tends toward formation of ureas (equation 30).



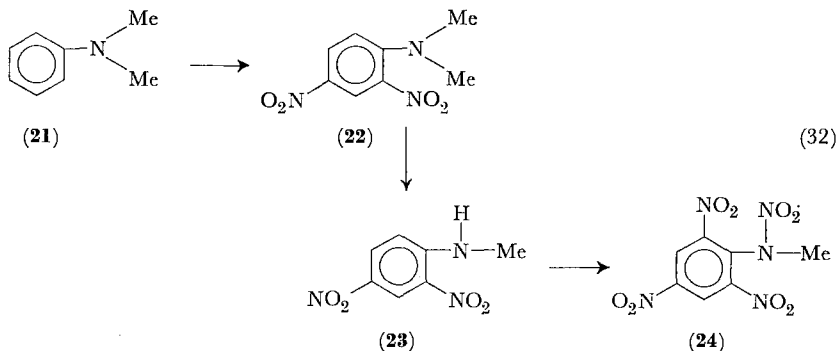
## V. SECONDARY NITRAMINES

Secondary nitramines are much more stable in highly acidic media than are primary nitramines, so direct nitration is feasible from this aspect. However, as will be noted later some secondary amines do not respond well to direct electrophilic nitration. For this reason the nucleophilic reaction of Angeli<sup>13</sup> has been used successfully for synthesis of secondary nitramines<sup>15,17</sup> (equation 31).



where B represents alkoxide or amine anion and  $R'NO_3$  an alkyl nitrate, cyanohydrin nitrate, nitril nitrate or nitril fluoride.

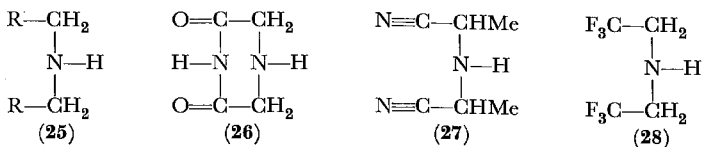
The nitration-oxidation of dimethylaniline (**21**) which leads to synthesis of 2,4,6-trinitrophenylmethylnitramine (**24**) is of general applicability in the formation of secondary polynitrophenylmethylnitramines<sup>57,58,59</sup>. Before or during the oxidation of the methyl group the aromatic nucleus is nitrated, (equation 32) to **22** and then oxidized



to dinitrophenylmethylnitramine (**23**), which is nitrated quickly to **24**, probably because the aromatic nitro groups make it a weak base. Although the conversion of *N*-methyl to *N*-nitro is applied principally to aromatic amines it has been observed also with saturated aliphatic amines<sup>59</sup>.

Only weakly basic amines can be nitrated directly. Those first shown to form nitramines in good yield are imino-*bis*-acetonitrile (**25**, R is  $C\equiv N$ ), imino-*bis*-acetic acid (**25**, R is  $COOH$ ), as well as its amide (**25**, R is  $NH_2-C=O$ ) and its cyclic imide<sup>60</sup> **26**. Later

$\alpha,\alpha$ -dimethyl-imino-*bis*-acetonitrile<sup>61</sup> (27) and imino-*bis*-2,2,3-trifluoroethane<sup>62</sup> (28) have been found to behave similarly. On the other hand more strongly basic amines such as diisopropylamine (29) in



which groups donate electrons to nitrogen, will not form a nitramine in nitric acid alone or with acetic anhydride.

According to titration with sulfuric or perchloric acid in acetic acid using *o*-nitroaniline<sup>63, 64</sup> as photo indicator a list of basicities has been compiled<sup>65</sup> and is presented in Table I. The level of basicity at which some nitramine formation with nitric acid alone or in the presence of acetic anhydride is observed, is found to be between 0.31 and 0.49 on the perchloric acid scale. A 93% yield of nitramine is obtained from 25 (R is C $\equiv$ N)<sup>66</sup> while a 22% yield is obtained from piperidine (41) and a 6% yield from dimethylamine<sup>67</sup> (35).

Some insight into this behavior may be gained by observation of the ultraviolet absorption maxima<sup>62</sup> and the extinction coefficients of the nitrate salts of these amines in acetic acid. The salts of the strong amines show (Table I) moderate absorption at 2960 m $\mu$  which is characteristic of metal salts that show nitrate as an ion or as part of an ion-pair in acetic acid. On the other hand the salts of the weak amines absorb characteristically at 2670 m $\mu$  in acetic acid (2700 m $\mu$  in absolute ethanol) which is identical with that of imperceptibly-ionized nitric acid in the same media. In other words the strongly basic amine in acetic acid is bound to all of the nitric acid (molecule or ion-pair) or else to the proton of the nitric acid (ammonium and nitrate ions) whereas the weakly basic amine exists separately from nitric acid in the acetic acid solution. This situation is peculiar to the medium, as well as to acetic acid containing a little acetic anhydride. In water the weakly basic amine nitrate shows spectral absorption similar to that of the strongly basic amine salts.

The situation in acetic acid which is indicated by spectral absorption is confirmed by electrical conductance and molecular weight determinations. The conductances of the strongly basic amines are sufficiently low to indicate that the salts are not appreciably ionized, but they are ten to twenty-fold greater than the conductances ( $\lambda = 0.02$ ) of the weakly basic amines. Since this is also the equivalent conductance of absolute nitric acid in acetic acid it is not

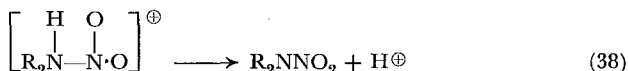
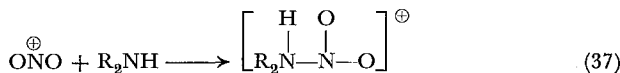
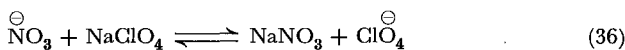
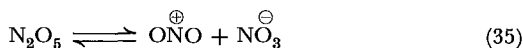
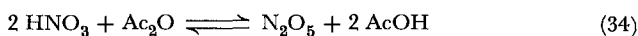
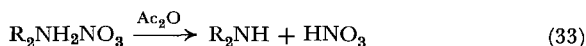
TABLE 1. Proton-attracting tendency with respect to perchloric and sulfuric acids, and to spectral absorption.

Number	Amine	Intensity colored indicator		$\lambda_{\max}$ $\pm 10 \text{ m}\mu$ $\text{\AA}$	$E_{\max}$
		Intensity total indicator			
		Sulfuric acid	Perchloric acid		
29	Diisopropylamine		0.68		6.6
30	Diisobutylamine	1.06	0.54		
31	Dicyclohexylamine	1.05	0.53		
32	Di- <i>n</i> -butylamine	1.04	0.53		6.8
33	Diethylamine	1.02	0.52		
34	Di- <i>n</i> -actylamine	1.02	0.52		
35	Dimethylamine	1.01	0.51		
36	Lysidine	0.99	0.50		
37	Methylethanolamine	0.98	0.50		
38	Diisoamylamine	0.95	0.49		
39	Morpholine	0.92	0.46	2960	7.6
40	$\beta$ -Imino- <i>bis</i> -propionitrile	0.85	0.43	2950	7.7
41	Piperidine		0.49	2960	8.1
42	Diallylamine			2960	8.1
43	Ammonia			2950	8.2
44	Dibenzylamine			2960	8.6
45	Diethanolamine				
25; R, C $\equiv$ N	Imino- <i>bis</i> -acetonitrile	0.77	0.40	2670	9.5
27	Imino- <i>bis</i> -methylacetonitrile diast. (m.p. 68°)		0.31		
27	Imino- <i>bis</i> -methylacetonitrile diast. (liq.)		0.18	2700*	
28	Imino- <i>bis</i> -trifluoroethane		0.08		9.3
46	Imino- <i>bis</i> -dimethylacetonitrile		0.14	2670	9.3
			0.08	2700*	9.5*

\* Determined in absolute ethanol which shifts  $\lambda_{\max}$  about 30 m $\mu$  to longer wavelength than is observed in acetic acid.

surprising to find that the freezing point lowering for the weakly basic amine nitrates in acetic acid indicates the nitric acid and the amine as separate particles. By contrast the strongly basic nitrates in acetic acid seem to exist largely as undissociated salts.

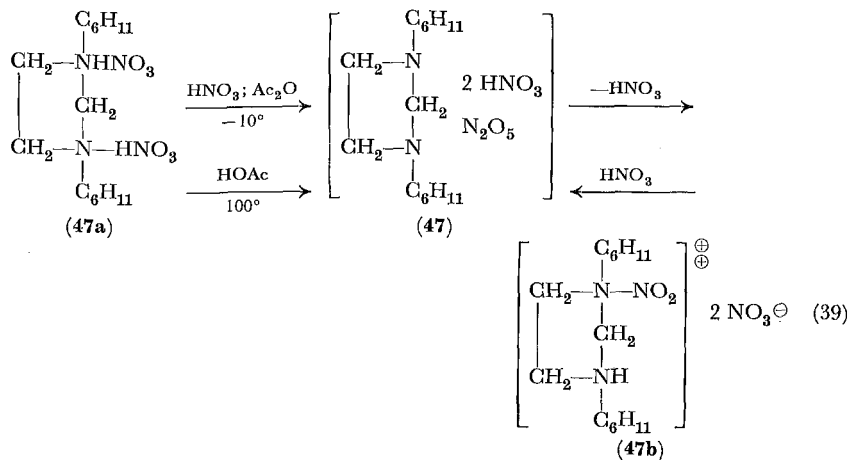
A kinetic study shows<sup>62</sup> that the nitration of the weakly basic amine salt in acetic anhydride-acetic acid is first order in amine and first order in nitric acid. Although the reaction is complicated by concomitant acetylation with formation of the *N,N*-dialkylacetamide, the rate is sufficiently constant to ascertain that it is increased by addition of perchlorate and depressed by addition of nitrate salts. This behavior, indicative of depression of ionization, may be interpreted as reversal of the formation from nitrogen pentoxide of nitronium and nitrate ions. The nitration may be described by steps 33–38.



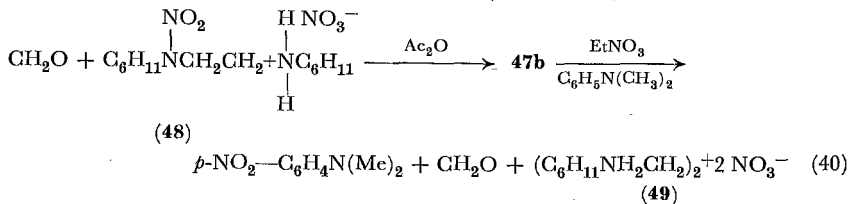
In this series, step 33 presents the state of the weak amine salt initially in acetic anhydride. According to step 34 the amount of nitrogen pentoxide generated will depend upon the acetic acid present, which indeed has been found to be the fact. The ionization of this nitrogen pentoxide in step 35, so slight that ordinarily it cannot be detected<sup>68</sup>, will be decreased by addition of nitrate ion or increased by addition of perchlorate which will depress the nitrate ion (step 36). In any case the nitronium ion concentration will be miniscule unless it is stabilized by complexing with water (to nitracidium ion) or with an amine (step 37). If water is absent the ammono-nitronium ion will predominate until it loses a proton to form the nitramine (step 38). Of course nitronium ion might also coordinate with acetic acid but in this event the acetatonitronium ion by proton loss will form 'acetylnitrate' which itself by exchange or ionization will be a source of nitronium ion.



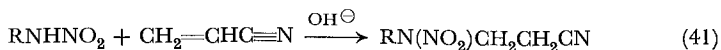
This is the reasonable theory. Since step 37 seems to be the rate-controlling step it is difficult to detect the complex cation. However, acetyl nitrate<sup>69</sup> and benzoyl nitrate are known to form complexes with tertiary amines in circumstances where step 38 cannot occur. In the later instance the complex **47**, is capable of nitrating phenol, dimethylaniline and imino-*bis*-acetonitrile (**25**). In these nitrations



the complex **47** might simply be acting as a source of dinitrogen pentoxide. But if this were the fact then dicyclohexyldiazacyclopentane dinitrate (**47a**) ought to be obtained as well (equation 39). Actually the other product is not **47a**, but, instead is *N,N*-dicyclohexyl-1,2-diaminoethane dinitrate (**49**). More likely the mononitronium-monoammonium salt **47b** (from **47** by loss of nitric acid) transfers nitronium ion to dimethylaniline (in ethyl nitrate medium) and receives from it a proton which causes hydrolysis to **49**. The alternative transfer of a proton from the di-cation of **47b** (to nitrate ion in the reaction medium) would result in the *N*-nitro-1,2-diaminoethane mononitrate **48**, by an analogous process which will later be discussed as 'nitrolysis'. Actually the formation of **48** from **47b** occurs in acetic anhydride. One may assume participation of **47b** in both nitration and nitrolysis (equation 40).



Because strongly basic amines form ammonium salts with nitric acid, apparently to the exclusion of nitronium salts, they cannot be nitrated directly to give secondary nitramines in satisfactory yield. Alternative methods such as diazomethane methylation of primary nitramines are inconvenient or unsatisfactory. Although primary nitramines partake well in the Michael reaction<sup>70</sup> to give secondary nitramines the reaction is of limited applicability (equation 41).



Perhaps the best alternative to nitration has been the oxidation of the analogous nitrosamine when available.

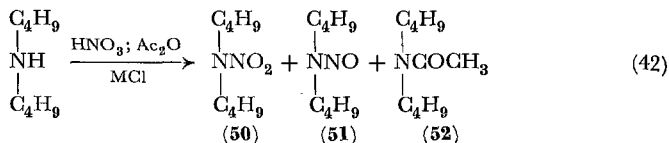
Originally this conversion of nitrosamines to nitramines was effected by use of hydrogen peroxide<sup>71,72</sup> and it suffered from a tendency for the nitrosamine to revert to the amine. However, the conversion may be carried out very efficiently by use of trifluoroacetyl peroxide<sup>73</sup>.

Although strongly basic secondary amines cannot be converted to the nitramines by nitric acid, alone or in acetic anhydride, the reaction does occur in these media in the presence of chloride. It is of interest that this discovery was made by inadvertence. In contravention of the strong-base rule, a secondary amine nitrate that was carelessly dried over calcium chloride was converted by acetic anhydride to the nitramine whereas the same salt dried *in vacuo* without desiccant would not react. Tests showed that some hydrogen chloride–nitric acid exchange had occurred. Subsequently it was shown that small amounts of chlorides would raise the yield of dimethylnitramine, originally reported by Bamberger and Kirpal<sup>74</sup>, from 5% to 65%. Since these authors did not suggest that their yields were small, it is intriguing to speculate whether their dimethylammonium nitrate–acetic anhydride system was contaminated with chloride.

Of course it is possible that Bamberger and Kirpal obtained good yields by other variations, say by use of elevated temperatures. For example Chapman and Lamberton<sup>75</sup> nitrated morpholine in 48% yield by use of ammonium nitrate and nitric acid in acetic anhydride at 65°. However, the chloride-catalyzed nitration of morpholine gives a 93% yield, so it would seem to be the preferred method.

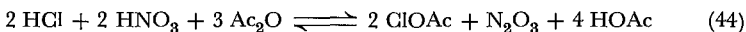
The chloride-catalyzed nitration in some instances yields besides the nitramine **50**, also the nitrosamine **51** and the acetamide **52** as byproducts. A typical example, dibutylamine, was studied intensively<sup>66</sup>. It was found that the slower the reaction the greater

was the yield of acetamide **52**, and that the more of catalyst was added to increase the rate of nitramine formation the greater was the yield of nitrosamine **51** (equation 42).



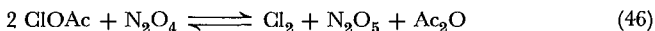
It was also found that the catalyst was lost in the form of molecular chlorine when the reaction system was vented to the atmosphere.

These facts led to an investigation which showed<sup>76</sup> that the chloride introduced into the system was oxidized by nitric acid to electropositive chlorine, notably chlorine acetate, with consequent reduction of nitric to nitrous acid. It appears that when the reaction system called Aqua Regia (equation 43) is carried out in acetic anhydride the products (equation 44) are different from those encountered in presence of water.



These are the principal reactions but other electropositive chlorine and nitrosonium salts also will be present<sup>77</sup>.

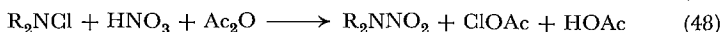
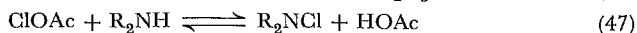
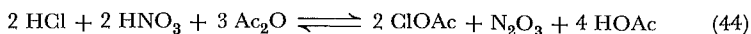
The presence of chlorine acetate in the reaction system used in nitrations at once suggested that a secondary chloramine would be formed when the amine was present. Accordingly a secondary amine hydrochloride was treated<sup>78</sup> with just enough nitric acid to fulfil the requirement of equation 42. The product was a mixture of the secondary nitrosamine and the chloramine. The chloroamine also was the product when the amine in acetic anhydride was treated with pure chlorine acetate but not when it was treated with chlorine. This observation is in correlation with the fact that catalytic amounts of chloride in the nitration system become ineffective when the reaction is a slow one. A path for conversion of the reactive chlorine acetate to unreactive chlorine was then sought and found kinetically in two slow reactions (45) and (46)<sup>78</sup>.



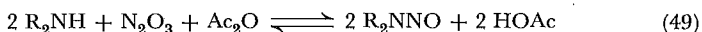
With this evidence at hand that chloramines are present in the  $\text{HCl}-\text{HNO}_3-\text{Ac}_2\text{O}$ -amine system, it remained to try the reaction of chloramines with nitric acid in acetic anhydride. Essentially the

same yields of nitramine are obtained as occurs when the amine is added to the chloride-catalyzed nitration system. The reaction involving chloramine may be written as equation 48, and the catalytic behavior of chloride may seem to involve the regeneration of chlorine acetate.

The chloride-catalyzed nitration of secondary amines is therefore a chain reaction which may be expressed by the chain-generating equation 44 followed by the chain-carrying equations 47 and 48,

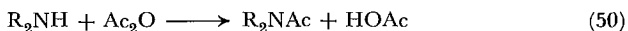


The slow chain-breaking step 45 will be minimized when steps 47 and 48 are rapid, but loss of catalyst described by reaction 46 is only minimized by the undesirable formation of the nitrosamine as a byproduct according to reaction 49. Even if the formation of nitrosamine were acceptable as a means of removing the nitrogen oxides (so that they could not react with chlorine acetate) the expedient would be impractical because reaction 49 is not chloride-catalyzed,



so it would be an ineffective scavenger. On balance, it is advisable to maintain a significant amount of catalyst so as to accelerate formation of nitramine at the expense of nitrosamine and to utilize the catalyst before it is destroyed by reactions 45 and 46.

The acetylation of the secondary amines is independent of the nitration and reaction 50 is not chloride catalyzed. Also it is slower

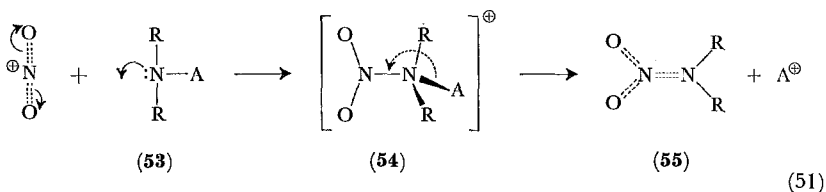


than nitrosation and catalyzed nitration, it is not troublesome unless the amine (when it contains secondary or tertiary alkyl groups) is so basic that reactions 47 and 48 are very slow.

For example, in the production of the practical explosive, dinitroxydiethylnitramine, which involves an amine of moderate basicity, the product does not contain a detectable amount of the acetamino derivative. The nitrosamine, which can be removed easily because it decomposes in boiling water, could not exceed 15% because 85–96% yields of pure nitramine are obtained consistently. But catalyst control is necessary. On one occasion during ton-lot production the operator, disturbed by the odor emanating from the reactor, removed the noxious fumes by suction. Actually he removed

chlorine by this device and his yield of nitramine was minimal. This practical experience might have been anticipated from the fact that reactions 44, 45, 46, 47, and 49 involve mobile equilibria which are easily shifted. Actually these equations are only a few of those which might be written to describe this complex system. The original reference should be examined for further detail.

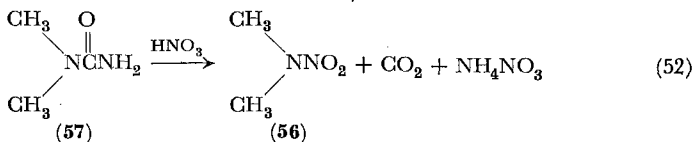
Presumably the chloramines are nitratable (when the parent amines are not) because they are weaker bases than the amine from which the chloramine is generated. The more stable (and also more symmetrical) the substituted ammonium ion (the protonated amine, free or as part of an ion-pair) the more will its overall-positive charge tend to repel an electropositive nitronium ion. However this explanation is not sufficient in view of the attack on the same ammonium ion by electropositive chlorine. Assuming that attack by either nitronium ion or cationic chlorine occurs with a small amount of free amine it is obvious that, unlike cationic chlorine, nitronium ion approaching the amine, as in **53** ( $A=H$ ) must bend out of its carbon dioxide structure (equation 51)



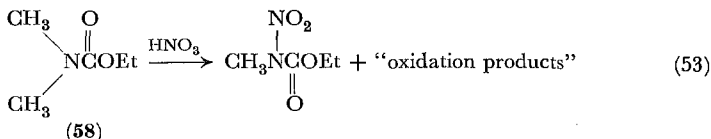
in order to form the complex ion **54**. The N—N bonding which will aid this process will be the greater if besides sigma bonding a contribution of pi bonding (ultimately the stabilizing influence in the nitramine **55**) is contributed by ejection of A. This ejection will be easier if A is Cl rather than H, according to the relative strengths of N—Cl and N—H bonds. Of course the over-all electron distribution in the ammononitronium ion **54**, also is involved, so it is not unexpected that the rate of nitration of secondary chloramines is slowest for those derived from the most basic amines.

Although the reduction in amine basicity by chloramine formation is a convenient way of nitration, the idea is not new. It has long been known that electron-attracting groups will make a *N*-substituted secondary amine less basic than the parent amine. Such substances may be 'nitrolyzed' by use of absolute ('real') nitric acid and sometimes with nitric-sulfuric acid systems. In fact the first dialkyl-nitramine **56** was prepared in this manner<sup>79</sup> and the substituted

urea **57** is the best reagent (equation 52).



Compound **56** is also obtained from tetramethylsulfamide<sup>80</sup>, *N,N*-dimethylethanesulfamide<sup>81,82,83</sup>, dimethylacetamide<sup>84,85,86</sup> and dimethylbenzamide<sup>87,88</sup>. However, with dimethylurethane (**58**) the reaction takes a different course<sup>89</sup> (equation 53),

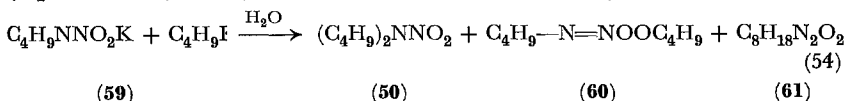


This reaction is frequently observed among the higher homologues of the dialkylacylamides, sulfonamides and even the ureides. Obviously it limits the use of the previously-mentioned reaction as a method of preparing secondary nitramines.

Nevertheless the reaction of negatively *N*-substituted dialkylamines is of interest in relation to more modern studies, especially since Franchimont observed early that the yield of secondary nitramine was directly related to the basicity of the parent amine. The reaction is not dissimilar to that of the chloride catalyzed nitration. In this connection it is noteworthy that *N-n*-butyl-*bis*-acetamide is recovered unchanged upon treatment with nitric acid in acetic anhydride. In such a system an anionic acceptor for an ejected cation is sparse.

## VI. SECONDARY ISONITRAMINES

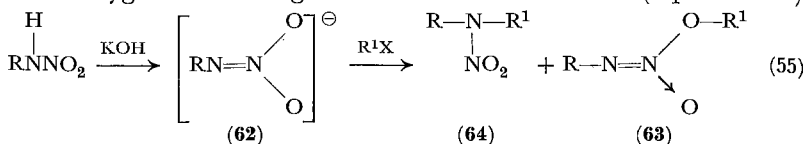
There has been little interest in these substances and not much is known about them. Indeed the structures have not been proved rigorously. They are formed during the alkylation of primary nitramines, especially in alkaline solution<sup>90,91</sup>. In the example cited (equation 54) the yield of di-*n*-butylnitramine (**50**) was 32 % b.p.



129–30 (11 mm) while that of dibutyliisonitramine (**60**) was 24 % b.p. 97–99 (11 mm), and 26 % of the parent butylnitramine, the acid of **59** was recovered<sup>68</sup>. Part of the loss is due to another isomer **61**

which is very unstable. Its type has been observed often<sup>92</sup> but never obtained pure. Decomposition products are nitrogen, hydroxyl and aldehyde-like substances<sup>37</sup>, the same as are obtained from isonitramines when they are heated with alkali. None of the parent primary nitramine (which is stable in alkali) is recovered upon acidification.

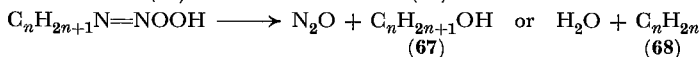
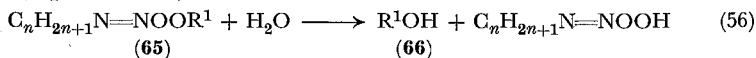
The ratio of nitramine **50** to isonitramine **60** is an average but it can vary from a preponderance of nitramine to isonitramine when 1,2-dinitraminoethane is methylated to the reverse with phenylnitramine<sup>32</sup>. The principal basis for assignment of structure **63** is the expectation that it will arise from the ion **62** where the charge between oxygen and nitrogen is resonance-distributed (equation 55)



Since the group 'R' will influence this distribution the relative attachment of R<sup>1</sup> to give **63** or **64** may be expected to vary among nitramines. Of interest is the fact that reaction with diazomethane usually gives the secondary nitramine uncontaminated with isonitramine but here too phenylnitramine<sup>28,29</sup> is an exception although 2-nitraminothiazole<sup>30</sup> follows the rule.

The products of alkylation may be classified easily by the Franchimont test. The isomers of unknown structure **61** in acetic acid with dimethylaniline show a green color before the customary addition of zinc dust but the isonitramine gives no color either before or after the addition of zinc. Contrary statements about isonitramines of ostensible purity (but obviously-contaminated) attest the isomeric nature of **61**.

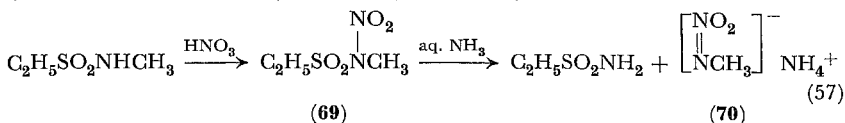
When a dialkyl nitramine is treated with 40% sulfuric acid no reaction occurs, but a quiet evolution of nitrous oxide takes place when a secondary isonitramine (**65**) is treated with this reagent<sup>91</sup>. In addition, alcohols **66** and **67** are found in the product. The alcohol **67** may also appear, in whole or part, as the alkene **68** and water. No doubt but it is significant that products **67**, **68** and water are obtained by the action of 40% sulfuric acid on primary nitramines<sup>93</sup> (equation 56).



But again phenylnitramine is an exception<sup>94</sup> because it gives nitrogen and nitric oxide. The isomers of unknown structure **61**, give nitrous oxide like the isonitramines.

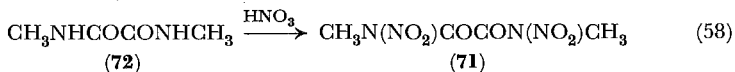
## VII. SECONDARY NITRAMIDES

Because they were the original source of primary nitramines the secondary nitramides were among the first of the *N*-nitro compounds. The nitration of ethylsulfonmethylanide<sup>83</sup> was found to proceed smoothly and in good yield. Nowadays this ease of nitration may be attributed to the weakly-basic nature of the imino group. Absolute ('real') nitric acid was used (equation 57),

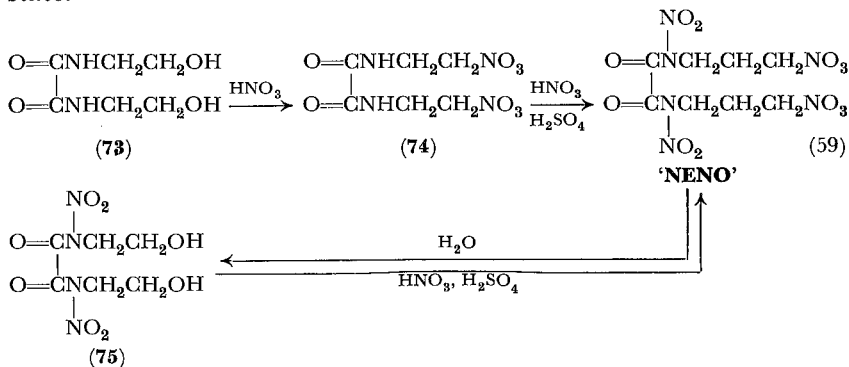


The nitramide **69** could be hydrolyzed by boiling water to give the primary nitramine at once or with ammonia at lower temperature to give the ammonium salt **70**.

The nitration-hydrolysis path is equally successful with urethanes<sup>86,87</sup> and with carboxylic acid amides. Some of the nitration products<sup>34,85,94</sup> have been considered for use as explosives; for example *bis*-methylnitraminoöxamide (**71**) from *symm.* dimethyl-oxamide (**72**) (equation 58) has been studied because its melting



point (124°) provides a convenient eutectic with trinitrotoluene and the solidified melt is free from gross cavities. However, it tends to decompose with gas formation when retained long in the molten state.

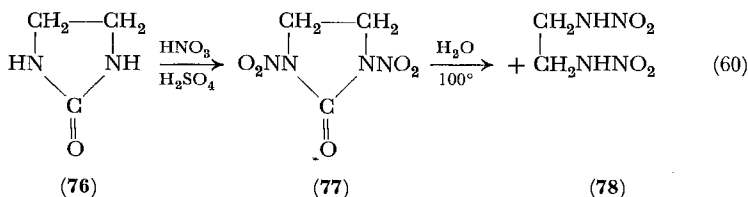




A more energetic nitramide intended for use as an explosive is *bis*-nitroxyethylnitroöxamide (NENO)<sup>95</sup> from *bis*-hydroxyethyloxamide (**73**) (equation 59). During a study of its manufacture<sup>96</sup> it has been found that only nitrate esterification occurs in absolute nitric acid to give a 98% yield of *bis*-nitroxyethyloxamide (**74**). Mixed nitric-sulfuric acid is required to convert **74** into NENO but the *N*-nitration is inhibited by 0.02 equivalent of nitrosylsulfuric acid. In absence of nitrous acid, **73** is converted to an 85% yield of NENO within 45 minutes but this yield decreases to 79% after 120 minutes. Probably a slow de-esterification is occurring in the spent acid to give *bis*-hydroxyethylnitroöxamide (**75**) although this compound has never been isolated. Its presence is inferred because the impure product of lower yield after 120 minutes of reaction time can be restored to maximum yield and purity simply by adding it to fresh mixed nitric-sulfuric acid.

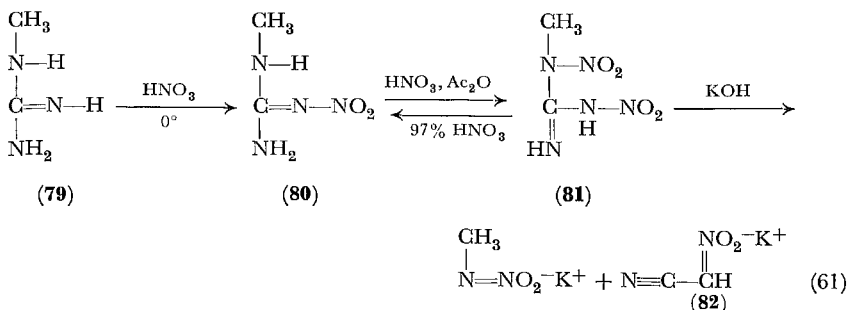
NENO has about the same explosive power and impact sensitivity as TETRYL. NENO has been studied as a replacement for TETRYL because it can be manipulated at 100° in the liquid state and its slow rate of crystallization from the cooled magma insures absence of voids in the resolidified explosive.

Just as ureas are related to amides so nitroureas resemble nitramides. The nitro group enters at the secondary amido position in monoalkylureas<sup>28</sup>. Many cyclic amides and diamides have been nitrated, of which 1,3-imidazolidone-2<sup>97</sup> (**76**) via the 1,3-dinitro-derivative (**77**) comprises a source of the powerful and stable explosive 1,2-dinitraminoethane (**78**) (equation 60).



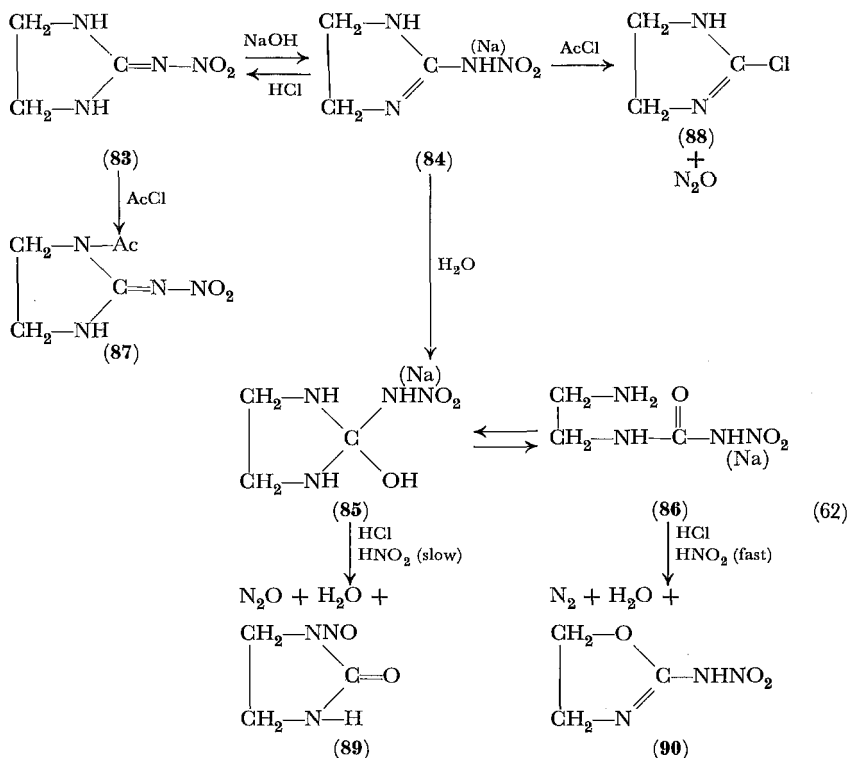
Nitroguanidines, as ammono-analogues of nitroureas, may be classified among the nitramides but much of the chemistry of nitroguanidines is different. As has been shown above, nitrourea behaves as an acid whereas nitroguanidine, being normally a nitrimide<sup>98</sup> does not. From the viewpoint of the explosives technologist this is important because acids like 1,2-dinitraminoethane (**78**) and picric acid may corrode their containers to form salts which are dangerous.

However, some nitroguanidines are normally in the nitramido rather than the nitrimido form. Typical is 1-methyl-1,3-dinitroguanidine<sup>99</sup> (**81**) which is prepared from 1-methylguanidine (**79**), *via* 1-methyl-2-nitroguanidine (**80**) (equation 61). The second nitro group, which must be introduced by use of acetic anhydride and



nitric acid, imparts properties different from that of compound **80**. It is partially denitrated in 97% nitric acid, which partly explains why it cannot be prepared in this medium. Also it decomposes readily in absolute nitric acid to give nitrous oxide. This may be a consequence of its fission to yield methylnitramine which is unstable in absolute nitric acid. The facility of the fission is shown by the ease with which methyldinitroguanidine (**81**) is split by alkali into the salts of methylnitramine and of nitrocyanamide (**82**). Perhaps the most profound effect of the second nitro group in **81** is its influence in shifting the nitrimido group in **80** to a nitramino group. This makes methyldinitroguanidine behave upon titration with alkali like a true acid whereas methylnitroguanidine (**80**) is neutral toward alkali.

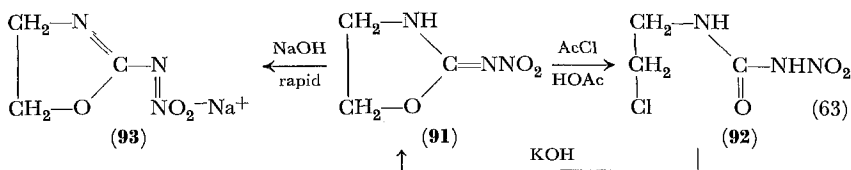
The nitrimides frequently isomerize to primary nitramides in alkaline solution. The first observation was made with nitroguanidine but a cyclic analogue has been studied more thoroughly<sup>56</sup>. The dipole moment of 2-nitrimino-1,3-imidazolidine (**83**) is that expected of a substance having the nitrimine structure<sup>100</sup>. It does not react with alkali at once in aqueous solution but during twelve hours the neutralization of the alkali indicates that the acidic 2-nitraminoimidazoline (**84**) has been generated. Acidification of this solution after twelve hours regenerates at least 20% of the original nitrimide **83** but the rest has been hydrated to the system 85–86 (equation 62). 2-Nitriminoimidazolidine and 2-nitraminoimidazoline thus are the pseudo-acid and aci-form, respectively.



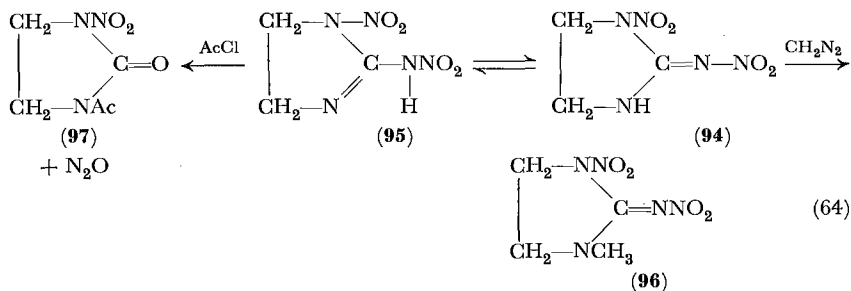
Further evidence for 2-nitriminoimidazolidine (**83**) as a pseudo-acid is found on treatment with diazomethane and acetyl chloride. The substance is inert toward diazomethane, which methylates all primary nitramines. It reacts with acetyl chloride to give 1-aceto-2-nitriminoimidazolidine (**87**) and not 2-chloroimidazoline (**88**) and nitrous oxide which is the expected reaction between acid chlorides and primary nitramines<sup>101</sup>. The nitrimide (**83**), also does not give the Franchimont color test with dimethylaniline<sup>32</sup>.

There is a certain vagueness in the definition of a pseudo acid. Hantzsch's historic example of nitroalkanes versus their aci-forms was wrongly extrapolated by him to the nitramine-isonitramine situation<sup>7</sup>. But as was shown by Euler<sup>23</sup> any transformation between the nitramine and isonitramine forms must be so rapid as to exclude them from Hantzsch's pseudo-aci definition. The same quandary appears as a matter of degree among the nitrimide-nitramide isomers. Substances like nitroguanidine and 2-nitraminoimidazolidine are properly to be classified as pseudo-acids because the transition to the

aci-form is slow. But other nitrimides may be converted rapidly. One of these is 1-aceto-2-nitriminoimidazolidine (**87**). This structure is attested by non-reactivity toward diazomethane and acetyl chloride. However, it behaves toward alkali as a weak acid ( $K_A = 1 \times 10^{-9}$ ). It is not to be classified as a pseudo acid if the latter is defined as a substance which is converted at a rate slower than that of ordinary titration. A similar instance has been encountered with 2-nitriminoöxazolidone (**91**) which is formed by the action of 1 equivalent of hot ethanolic alkali on  $\beta$ -chloroethyl-3-nitrourea (**92**), and which reverts to it (without loss of the nitramino group) upon treatment with acetyl chloride. (equation 63). If the product from **92** were the nitramine of which (**93**) is shown as the sodium salt then it should have lost nitrous oxide upon treatment with acetyl chloride.



Confusion arose<sup>102</sup> with 1-nitro-2-nitriminoimidazolidine (**94**) until the distinction between slow (pseudo-aci) and rapid (tautomeric) isomerism was understood. This substance, prepared by nitration of nitriminoimidazolidine (**83**) was first designated as the nitramide **95** for three reasons. First it behaved in alkali as a true acid of moderate strength ( $K_A = 3 \times 10^{-7}$ ). Secondly it reacted readily with diazomethane and thirdly it decomposed in strongly acid media with formation of nitrous oxide (equation 64). However,



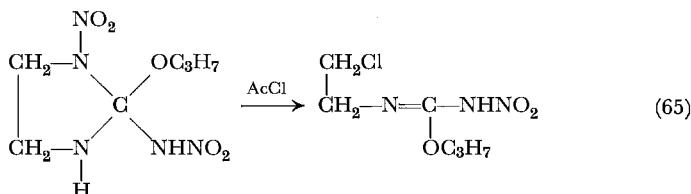
the dipole moment ( $\mu = 7.65$  D) found by Kumler<sup>100</sup> leaves little doubt that the substance itself is the nitrimide (**94**). Reviewing and revising the former proofs<sup>102</sup> it has been shown<sup>103</sup> that the action of diazomethane yields a highly explosive mixture of derivatives

from which 30% may be designated as 1-nitro-2-nitrimino-3-methylimidazolidine (**96**). Although the dinitro compound does react with acetyl chloride to give nitrous oxide and 1-aceto-3-nitroimidazolidone (**97**), the reaction conditions are abnormal for test purposes. Finally, although the rapid reaction with alkali does exclude 1-nitro-2-nitriminoimidazolidine (**94**) from the pseudo-acid class it does not preclude its original existence as a nitrimide which reacts rapidly with alkali to form the nitraminate.

Another aspect of the cycloguanidine chemistry which has caused some confusion<sup>101,104,105</sup> involves the consequence of a characteristic solvation reaction. An example is seen in the hydration either of the aci-form **84** of 2-nitriminoimidazolidine (**83**) or of **83** itself. The hydration product may be either 2-hydroxy-2-nitraminoimidazolidine (**85**) or 3 $\beta$ -aminoethyl-1-nitrourea (**86**). The product displays a dissociation constant ( $K_A$ ) of about  $3 \times 10^{-10}$  whereas most of the nitroureas are much stronger acids ( $K_A$  about  $10^{-4}$  to  $10^{-5}$ ). On this basis the substance might be specified as **85** but other evidence is equivocal. Nitrous acid ought to cause a ready evolution of nitrogen from the primary amino group of **86** but this gas does not appear for fifteen minutes after a two-fold excess of sodium nitrite-hydrochloric acid is introduced. The product is the 2-nitramino- $\delta$ oxazoline (**90**) expected if the amino group of **86** were converted to hydroxyl which then underwent cyclodehydration. On the other hand when a four-fold excess of sodium nitrite is added during twelve hours there is little evolution of gas until the end of this period. Moreover this gas is nitrous oxide rather than nitrogen and the product in good yield is 1-nitrosoimidazolidone-2 (**89**). This is the compound expected from **85** by *N*-nitrosation followed by decomposition of the nitramino group. It would seem that the hydration product of 2-nitriminoimidazolidine exists as 2-hydroxy-2-nitraminoimidazolidine (**85**) which is in mobile equilibrium with the non-cyclic 2- $\beta$ -aminoethylnitrourea (**86**) (equation 62). This variation of tautomerism has been defined as 'ring-chain' isomerism. It has been suggested<sup>106</sup> that the isomer actually in hand shall be classified whether 'ring' or 'chain' after consideration of its acid dissociation constant. However, this definition must be qualified by the observation that nitrogen is released slowly, even when the product of this gas-release arises from the chain isomer. Such phenomena indicate that the chain isomer may be held in a six-atom quasi-cyclic state by a hydrogen bond type of association which is

spatially as favorable as the five-atom cycle of the ring isomer. This geometry will be reflected in the dissociation constant.

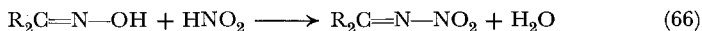
Products of solvation are also obtained from 1-nitro-2-nitrimino-imidazolidine (**94**)<sup>105</sup>, and in each instance the choice of isomer (ring and either nitrimido or nitramido chain) must be made. The product of ammonia addition includes a very labile ring<sup>103</sup>, while the dual point of the product from **94** and n-propylamine seems to indicate that the ring is stable at ambient temperatures but the nitrimido chain is stable at higher temperature<sup>106</sup>. When n-propyl alcohol (among others) is added to **94** the product is cyclic but another type of ring cleavage (with acetyl chloride) occurs in some of its reactions<sup>106</sup> (equation 65). Thus it may be seen that the



reactions of the so-called cycloguanidines are very diverse. However, it seems to be the fact that in the isolated state they are cyclic. The ring seems to be maintained in some solution media but not in others. The ring versus chain status will depend upon substituents and environment. Contrary conclusions have been drawn on the basis of absorption spectra but they are inconsistent and not in accord with the chemical evidence<sup>106</sup>.

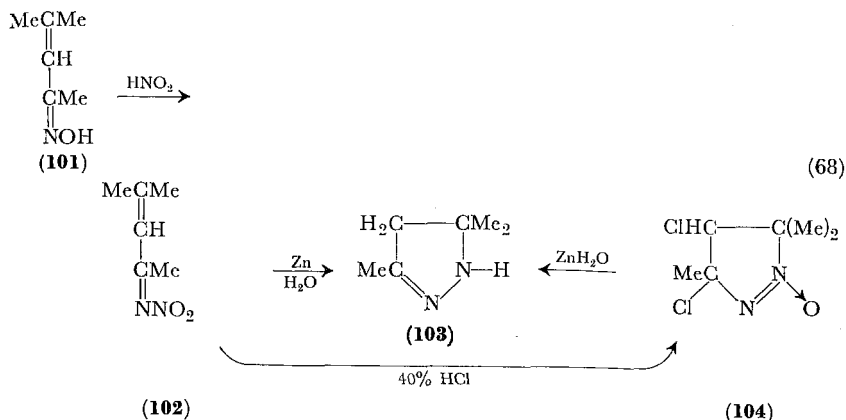
## VIII. NITRIMINES

Nitrimines were first discussed in 1895 but there has been doubt about the assignment of this structural unit. The substances are prepared by reaction of some oximes with nitrous acid (equation 66).



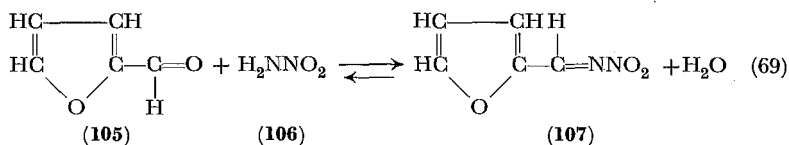
Angeli, who examined camphoroxime and other terpenoid ketoximes<sup>107</sup> called them 'pernitroso' derivatives of structure  $\text{R}_2\text{C}=\text{NONO}$  or  $\text{R}_2\text{C}=(\text{NO})_2$ . When Scholl used the oxime from pinacolone he specified the product as the nitrimine because *inter alia* it did not react with diazomethane. However, it could be converted to a sodium salt and thence to other salts. Since treatment of the





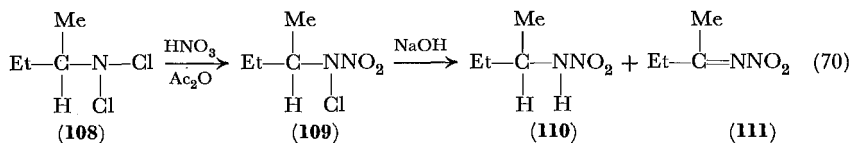
by being soluble immediately in cold alkali. When this solution is acidified the precipitate, probably the nitramine, is isomeric with the nitrimine to which it slowly reverts.

Three other methods have been found for preparation of specific nitrimines. First of these is a direct condensation of furfural (105) with nitramine (106)<sup>107</sup> (equation 69).



The reaction is one of mobile equilibrium tending strongly toward the left and it is unsuccessful with many aldehydes and ketones which have been studied, including camphor and mesityl oxide. The unfavorable equilibrium may explain that nitrimine formation has not been observed by nitrosation of the oximes of furfural and benzaldehyde. Such products, if formed, would tend to decompose to the aldehyde and nitramine, which is unstable in acidic media.

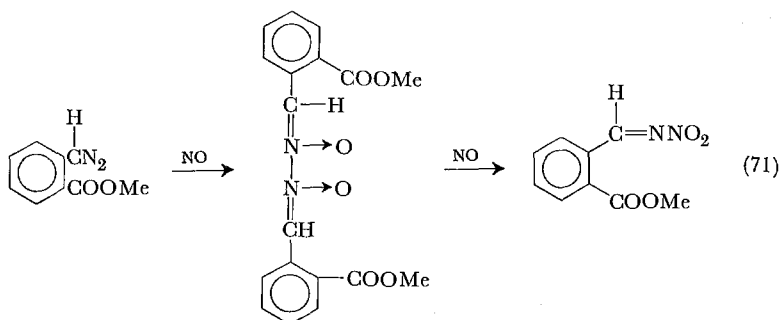
A second method for preparation of nitrimines is a variation of the preparation of primary nitramines from dichloramines and it has not been developed thoroughly<sup>21</sup>. When *sec*-butyldichloramine (108) is treated with nitric acid and acetic anhydride the chloronitramine 109 is formed (equation 70),



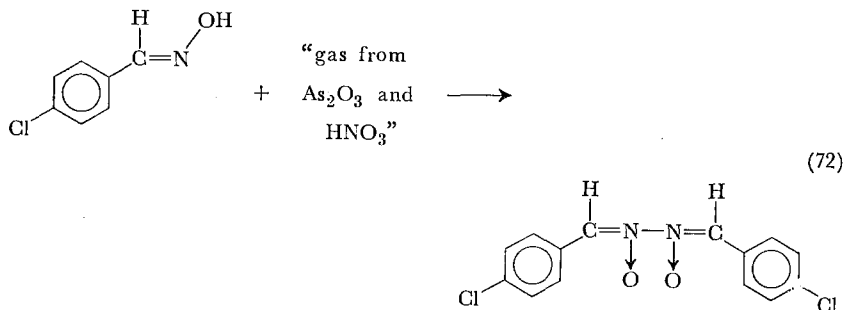


If instead of a reducing agent **109** is treated with aqueous alkali both the nitramine **110** and the nitrimine **111** are formed. They may be separated because the nitramine **110** unlike the nitrimine **111** is soluble in alkali.

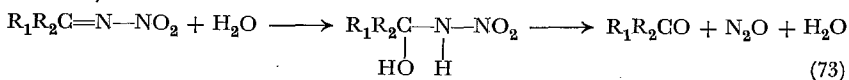
A third method for preparation of nitrimines, reported by Kirmse<sup>180</sup>, depends upon the reaction of nitric oxide with diazoalkanes. Kirmse believes that this reaction proceeds via the azine dioxide. Typically when 2-carbomethoxybenzyl diazomethane is treated with nitric oxide the first product is 2-carbomethoxybenzalazine dioxide which reacts with more nitric oxide to give 2-carbomethoxybenzalnitrimine (equation 71).



It is of interest that Kirmse also has synthesized the azine dioxides from the same sources (the oximes) as was used by Angeli (equation 72).



Many nitrimines are unstable in aqueous media. The presence of butanone-2 among the products when **108** is converted to **110** and **111** shows that the low yield of **111** is due to its hydrolysis (equation 73)



As might be expected the carbonyl-containing product will be captured by a phenylhydrazine. As with **111** the reaction of phenylhydrazine with furfuralnitrimine (**107**) and camphornitrimine causes evolution of nitrous oxide and formation of the hydrazones. On the other hand the ostensible nitrimines **102** and **98** from mesityl oxide and from pinacolone respectively, do not react.

All of the candidates for nitrimine structure give a positive, although ephemeral, Franchimont test for *N*-nitro with dimethylaniline. However, the behavior toward alkali is different. Obviously furfuralnitrimine as such is not acidic. Neither 2-nitriminobutane (**111**) nor the  $R_2N_2O_2$  derivatives from mesityl oxide or pinacolone are soluble in cold alkali but the latter two dissolve without decomposition when the system is warmed. On the other hand camphornitrimine forms a potassium salt easily.

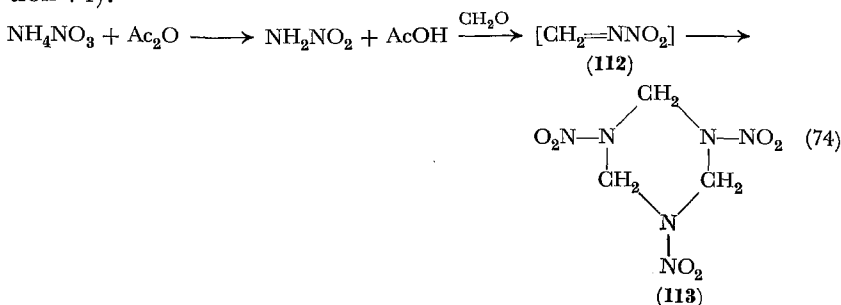
From a consideration of these data it would appear that Scholl and Harries were correct in their assumption that all of the substances of which they were speaking are nitrimines. The marked difference in stability may be attributed to hydration, which would be difficult in the hindered 3,3-dimethyl-2-nitriminobutane (**98**). This hindrance would not preclude the alternative protonic shift leading to the sodium salt **98a** although the transition might be such that strong alkali would be required. In short **98** may be a pseudo-acid. On the other hand 2-nitriminobutane is so easily hydrated that it decomposes before it can assume an aci-form. Intermediate between these is camphornitrimine which is not a pseudo-acid since it is converted readily to the nitramine salt.

In summary, the chemistry of the nitrimines is not unlike that of the nitrimides except that in general the latter are more stable. Perhaps this is not surprising because the amide or amidine group solvates less readily than does the carbonyl group in aldehydes or ketones.

## IX. POLYNITRIMINES

In the early days of World War II information was received *via* the British Intelligence Service that the Germans manufactured the explosive cyclonite (**113**) by a novel method involving ammonia, nitric acid, formaldehyde and acetic anhydride. From contemplation of these ingredients Ross and Schiessler<sup>109</sup> predicted that ammonium nitrate and paraformaldehyde in acetic anhydride ought to produce

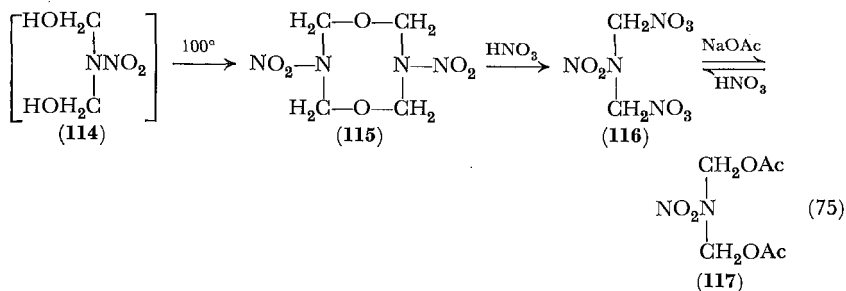
methylenenitrimine (**112**) which would trimerize to **113** (equation 74).



When they attempted this synthesis they found it to be successful to the extent of 35% yield on the formaldehyde basis. After the War it was found that the secret process of Eble<sup>109</sup> had indeed been duplicated by Ross and Schiessler. However, the reasoning which led to this success is now known to be faulty. There is no factual basis for the existence or intermediacy of methylenenitrimine. The achievements that arise from incorrect assumptions are notable examples of equivalence in the philosophy of science and are not carelessly to be deprecated.

Until it was realized that methylenenitrimine could not be an intermediate in the synthesis of cyclonite, many attempts were made to synthesize it<sup>110</sup>. When nitramine is treated with aqueous formaldehyde its characteristic instability in acid media decreases but not due to formation of **112**. Instead this stabilization seems to be due to formation of dimethylnitramine (**114**) although this compound has not been isolated in a pure state. However, it has been characterized by vacuum-evaporating its aqueous solution of preparation to leave a thick oil which on dehydration at 100° leaves 3,7-dinitro-3,7-diaza-1,5-dioxacyclooctane (**115**)\*. The ether linkages of this substance were cleaved by absolute nitric acid to give dinitroxydimethylnitramine (**116**) (equation 75). Since this nitrate ester could be converted to and regenerated from the diacetoxo analogue **117** the identity of dimethanolnitramine, (**114**) would seem to be established.

\* First prepared by F. C. Whitmore and C. I. Noll and reported to the author by private communication from Professor F. C. Whitmore, under whose chairmanship a working committee of chemists in the United States and Canada developed the detailed chemistry of cyclonite formation in 1941-1943. Much of the work was never published by the original workers but experimental repetition may be found in *Can. J. Res.*, **27B**, 218, 426, 469, 489, 503, and 520 (1949).

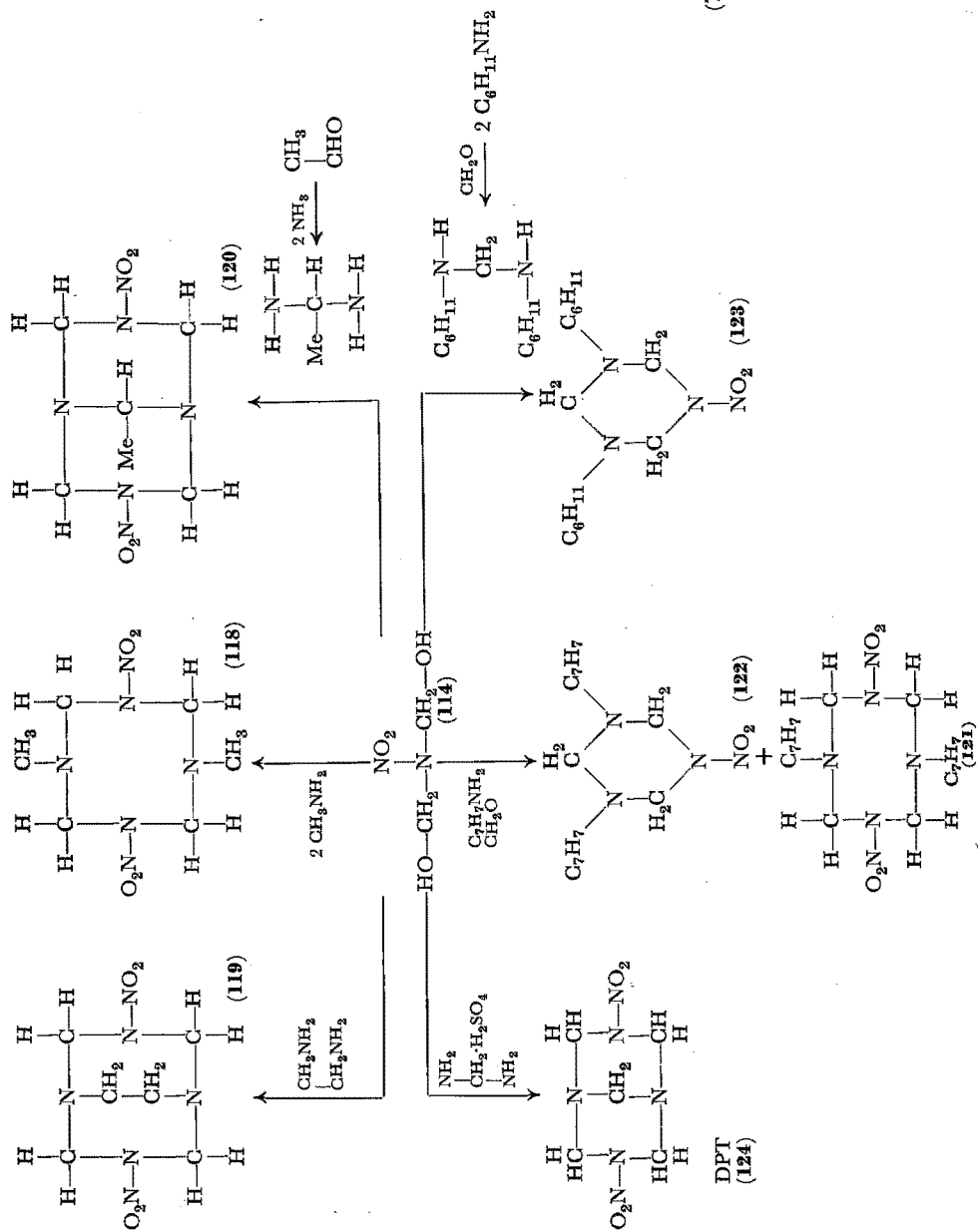


The aqueous solution containing **114** is a versatile system (equation 76). When it is treated with methylamine the precipitate is 1,5-dimethyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane (**118**), even when an excess of formaldehyde is present. A similar reaction occurs with 1,2-ethanediamine to form the bridged 3,7-dinitroendoethylene-1,3,5,7-tetrazacyclooctane (**119**). Indeed **114** can capture non-isolable substances such as 1,1-ethanediamine (from acetaldehyde and ammonia) by forming the bicyclic 1,5-endoethylidine-3,7-dinitro-1,3,5,7-tetrazacyclooctane (**120**). Thus two types of cyclization can occur: either with an amine or with an amine-aldehyde complex. It may be seen that benzylamine forms both types. Together with formalin it reacts with **114** as the free amine to form 1,5-dibenzyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane (**121**) and as dibenzylaminomethane to give the 6-membered cyclic 1-nitro-3,5-dibenzyl-1,3,5-triazacyclohexane (**122**). Cyclohexylamine also gives a triazacyclohexane but none of the tetrazacyclooctane. The formation of this 1-nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane (**123**) has been used to detect **114** in reaction liquors. Finally the solution of **114** has been treated with the sulfate of methanediamine known as Knudsen's salt to give the important derivative, 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetrazacyclooctane (**124**, called DPT). Despite this facility to combine with aldehydes and amines there is no indication that **114** will cleave in order to combine with itself to give cyclonite (**113**). Therefore, like methylenenitrimine, it cannot be considered to be an intermediate in formation of **113**. However, it is involved in the synthesis of **113**.

### A. Polynitrimines from Nitric Acid

The original<sup>111</sup> method of cyclonite synthesis was developed by Hale<sup>112</sup> on a practical basis. This so-called Hale process involves the treatment of hexamethylenetetramine (**125**) with a 20 mole

(76)



excess of absolute nitric acid. After filtration of crude **113** (80 % yield), the filtrate, neutralized to pH 5, will precipitate an 18 % yield of crude **124**. After removal of **124** an ether-extract of the remaining solution gives on evaporation an oil rich in formaldehyde. When this is treated with cyclohexylamine the formation of **123**, is presumptive for dimethanolnitramine (**114**).

Compound **124**, the first of these byproducts gives some insight into the nature of the process. It is evident that the conversion of **125** into **124** takes place though a solvolysis which Professor R. P. Linstead has named nitrolysis. However, in view of the large excess of absolute nitric acid in the reaction, the participation of nitronium ion or one of its solvates would be expected. Fission thus involves the

generation of a carboammonium ion  $\left[ \text{CH}_2 - \overset{\text{N}}{\overset{|}{\text{---}}} \right]^{\oplus}$  from nitronium

within the amine-solvated nitronium ion,  $\left[ \overset{\text{N}}{\overset{|}{\text{---}}} - \text{CH}_2\text{NO}_2 \right]^{\oplus}$ .

If the carboammonium ion acquires a nitrate ion ( $\text{X} = \text{NO}_3$ ) it is

stabilized as the nitrate ester,  $\overset{\text{N}}{\overset{|}{\text{---}}} - \text{CH}_2\text{X}$ , but if it acquires a hydroxyl

ion the resulting methanolamine is subject to acquisition of nitro-

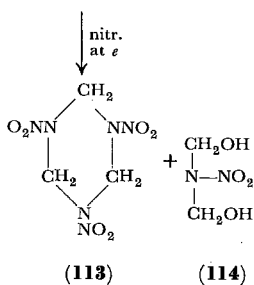
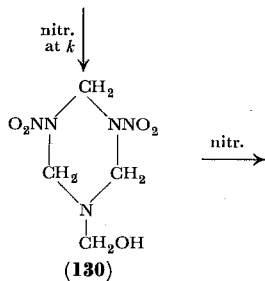
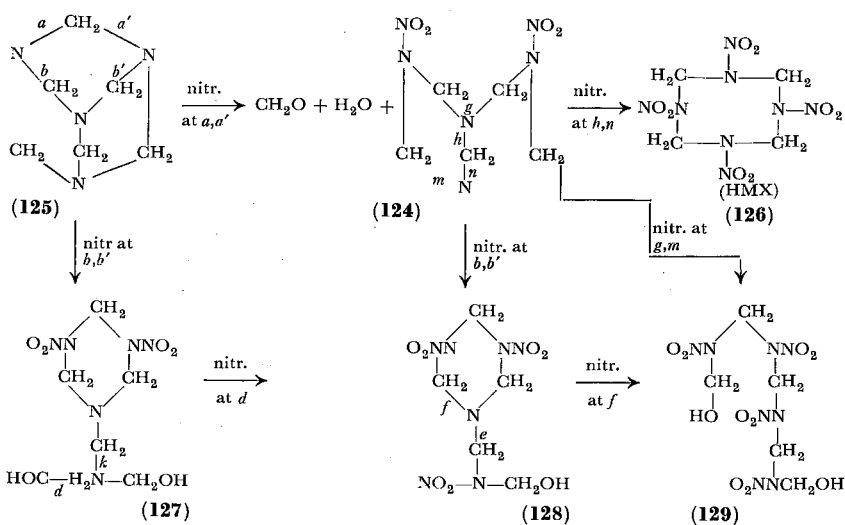
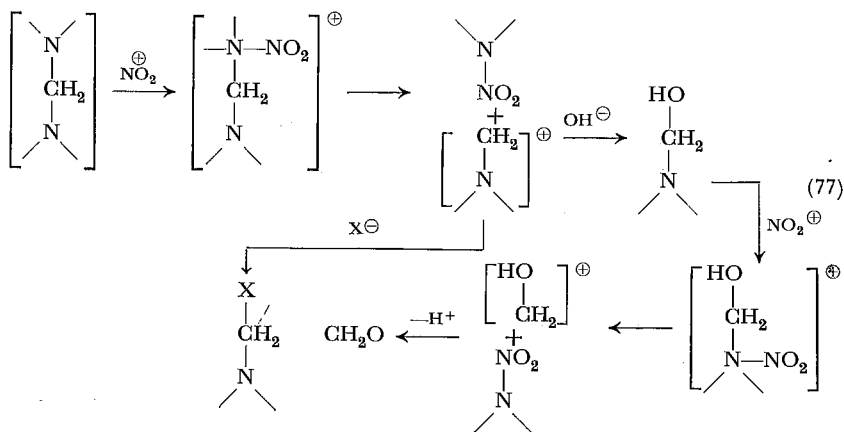
nium ion. This complex ion,  $\left[ \text{HOCH}_2 - \overset{\text{N}}{\overset{|}{\text{---}}} - \text{NO}_2 \right]^{\oplus}$ , will dis-

integrate into a nitramine and carboxonium ion,  $[\text{HO} - \text{CH}_2]^{\oplus}$ , which by loss of proton leaves formaldehyde (equation 77).

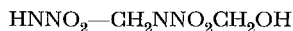
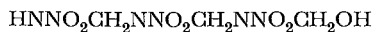
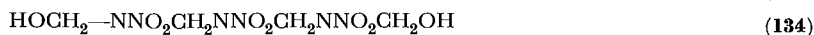
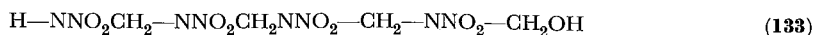
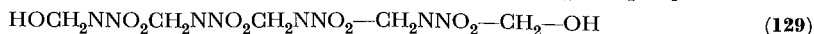
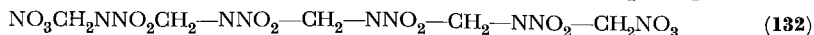
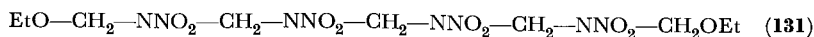
It is evident that this nitrolysis may involve other bonds of **125**, than *a*, *a*<sup>1</sup>. For example the fission of *b* and *b*' in **125** (equation 78) will lead to **127** which on nitrolysis at *d* will form 3,5-dinitro-3,5-diazapiperidymethyl-*N*-hydroxymethylnitramine (**128**). Nitrolysis of **128** at *e* leads to **113** and **114**. Therefore the latter substance is probably a final product and not a unit of synthesis. In other words **113** is formed by fragmentation and not by construction.

Not all of the intermediate fragments are isolable, but good evidence can be obtained to demonstrate their presence.

For example if **128** were to be nitrolyzed at *f* rather than *e*, then 1,9-dihydroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (**129**) would be formed (equation 78). This would be expected to 'unravel' rapidly by demethylation (equation 77) and primary nitramine



decomposition (equation 11) until finally **114** remains. However,



if nitrate ester formation occurs, **129** will be somewhat stabilized. Actually the dinitroxy derivative **132**, seems to survive to a slight extent in the reaction system and it can be detected by a useful reaction wherein the nitrate ester is converted to the ethoxy derivative **131**<sup>113</sup>. The detection is accomplished by boiling crude **113** in absolute ethanol and then isolating the relatively stable **131**.

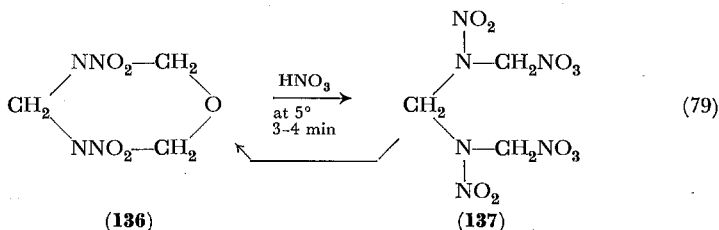
It may be noted that **129** or its dinitroxy analogue **132** could also arise by nitrolysis of **124** at *g* and *m* (equation 78). This is a preferred method of preparation<sup>114</sup> from this source by use of nitric acid containing dinitrogen pentoxide (so-called 106 % nitric acid) but **132** may be obtained in lower yield by use of 99 % acid. Therefore the alternative path *via* **124** might account for the traces of **132** in 'Hale cyclonite'. Indeed the fragmentation of **125** may be expected simultaneously to occur by several paths.

The exact conditions which favor one or the other of reaction paths are not well understood. It has been shown above that **124** is converted to a different cyclic polynitramine **126** by 99 % nitric acid but in '106 %' nitric acid **124** is converted to **132**. Also it was mentioned that in the nitrolysis of **125** by 99 % nitric acid **132** may be detected. If **125** is treated with 106 % nitric acid, **113**, obtained in low yield, is contaminated with a byproduct which is separated by treatment with boiling methanol or ethanol. In this way one can isolate the dimethyl or diethyl ether of 1,7-dihydroxy-2,4,6-trinitro-2,4,6-triazaheptane (**134**). The esters are presumptive for the dinitrate ester of **124** because the reaction,  $\text{R}-\text{NNO}_2\text{CH}_2\text{NO}_3 + \text{R}^1\text{OH} \rightarrow \text{HNO}_3 + \text{RNNO}_2\text{CH}_2\text{OR}^1$  is well established.

It may be noted that the 1,7-dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane is next lower than the tetrazaanonane **132** in a homologous series with the  $\text{CH}_2-\text{NNO}_2$  as the constant of homology.



The next lower member of the series (the dinitrate ester of 1,5-dihydroxy-2,4-dinitro-2,4-diazapentane (**135**) has not been detected in Hale reaction systems but it has been prepared by treatment of another byproduct of the system with nitric acid at 5°. When the Hale reaction system is slowly added to 28 % ammonia the formaldehyde present is converted into **125**, which may be extracted by hot chloroform after **113** is filtered off. When this chloroform solution is evaporated to a small volume the byproduct, 3,5-dinitro-3,5-diaza-1-oxacyclohexane (**136**) separates. This substance is probably not present in the reaction system because it is converted by 99 % acid at 5° to 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane (**137**)<sup>115</sup> and therefore should not survive the Hale conditions equation 79). More likely **136** (commonly called cyclonite oxide) is formed during the



dilution and neutralization process from **137**, but this reaction has not been examined.

The final member of this homologous series *bis*-nitroxymethylnitramine (**116**), might as the nitrate ester of **114** be expected in the Hale system. It has not been detected positively, perhaps because it precipitates with **113** upon dilution and is lost by decomposition before **113** is processed further. In any case it seems not to be the precursor of **114** because its rate of hydrolysis in neutral or slightly alkaline medium is too slow to account for **114** which can be extracted from such media.

It is significant that among the byproducts of the Hale nitrolysis there are no primary nitramines, which are known to be unstable in strongly acidic media. Only secondary nitramines in which the primary nitramino group is blocked by a methylol group or its ester are found. However, the stability of these methanolated fragments is only relative. Their presence in the reaction system, especially when it is slightly diluted with water, presents a hazard because the potential presence of formaldehyde and primary nitramines (equations 77 and 12) together with nitric acid constitute a system prone to explosive decomposition when nitrous acid is present. In water

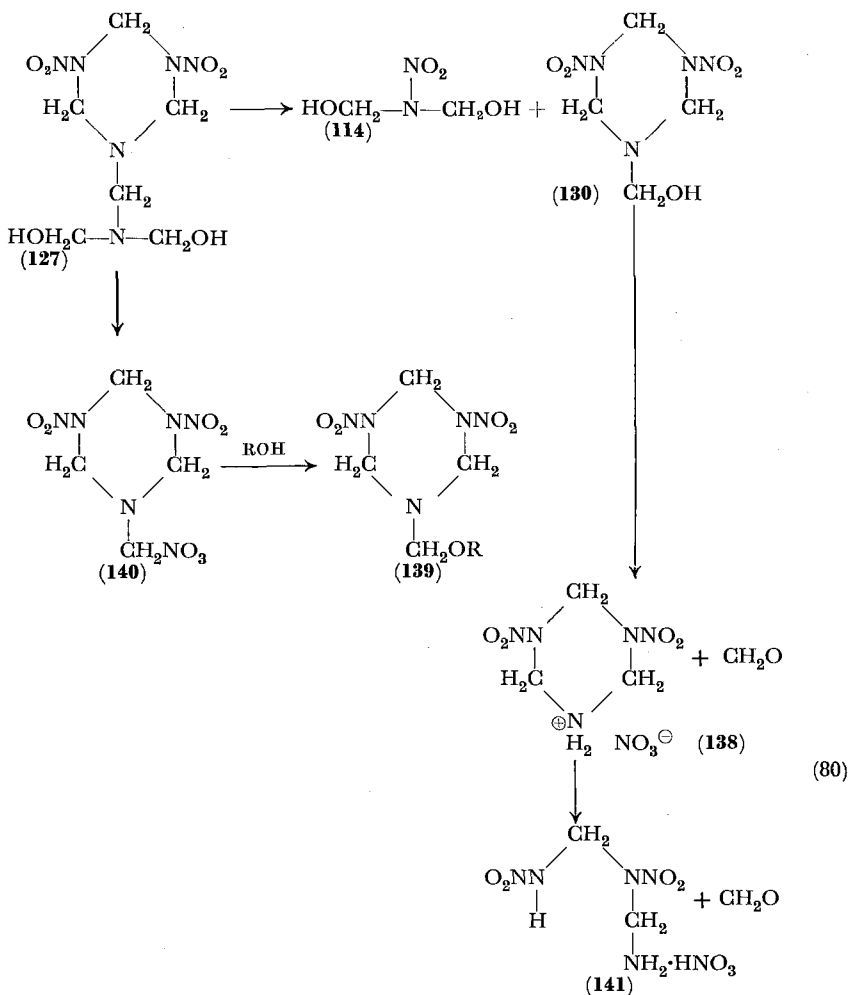
the methanolnitramines suffer hydrolysis rather than nitrolysis and the formaldehyde concentration 'builds up' until violent evolution of dinitrogen tetroxide occurs. In one industrial installation an attempt was made to stabilize these dilution liquors by use of hydrogen peroxide to prevent nitrous acid formation but reliance on this inhibitor resulted in loss of the plant. Henceforth it has been customary to allow the liquors to 'fume off' simultaneously with dilution. Thus not only the primary fragments are destroyed, but also methylene dinitrate and dinitroxydimethyl ether, which cause cardiac disturbance, are destroyed. The cyclonite is very stable so it survives this violent oxidation.

The resulting **113** ought to be pure but it contains an impurity as stable as itself. The contaminant, disconcerting because of the increased impact sensitiveness that it imparts to **113**, is HMX (**126**)\*, the most brisant known explosive because of its high energy and density. Its formation from **124** is obvious through nitrolysis at *h* and *n* (equation 78). It may be prepared in practical yield by nitrolysis of isolated **124** or from **120**<sup>114</sup>.

Despite many attempts to isolate all of the nitrolytic fragments from **125** neither **128**, **127** nor **130** have been isolated. However, good evidence for the last two compounds has been adduced by a low temperature variation of the Hale reaction (equation 80). When **125** dinitrate (the stable salt) is added to a 47 mole excess of 88–100 % nitric acid for 1–2 minutes at about  $-40^{\circ}$  and the system is then drowned in water, a clear solution is obtained. Within about one minute a precipitate appears which is 3,5-dinitro-3,5-diazapiperidinium nitrate (**138**)<sup>116</sup>. This substance seems to be formed via **130**. It would appear that upon dilution with water demethylation occurs to leave **138**.

Compound **138**, probably is not an intermediate in the formation of **113** from **125**, but evidently **130** does participate<sup>117</sup>. When a reaction system at low temperature comprised of **125** and nitric acid after a few minutes is diluted by addition of diethyl ether a gum precipitates. Treatment of this gum with ethanol yields 3,5-dinitro-3,5-diazapiperidylethoxymethane (**139**) (*R* = Et), which according to the established conversion is presumptive for dinitrodiazapiperidylmethylethyl nitrate (**140**) in the reaction system (equation 80). The only

\* Called HMX because of its high melting point. Many of these codified initials were used for ostensible secrecy during World War II and are found in the chemical literature. Thus cyclonite is abstract-listed as RDX (Research Department Explosive) and 1,7-endomethylene-3,5-dinitro-1,3,5,7-tetrazacyclooctane, (**124**) is listed as DPT or DNPT.

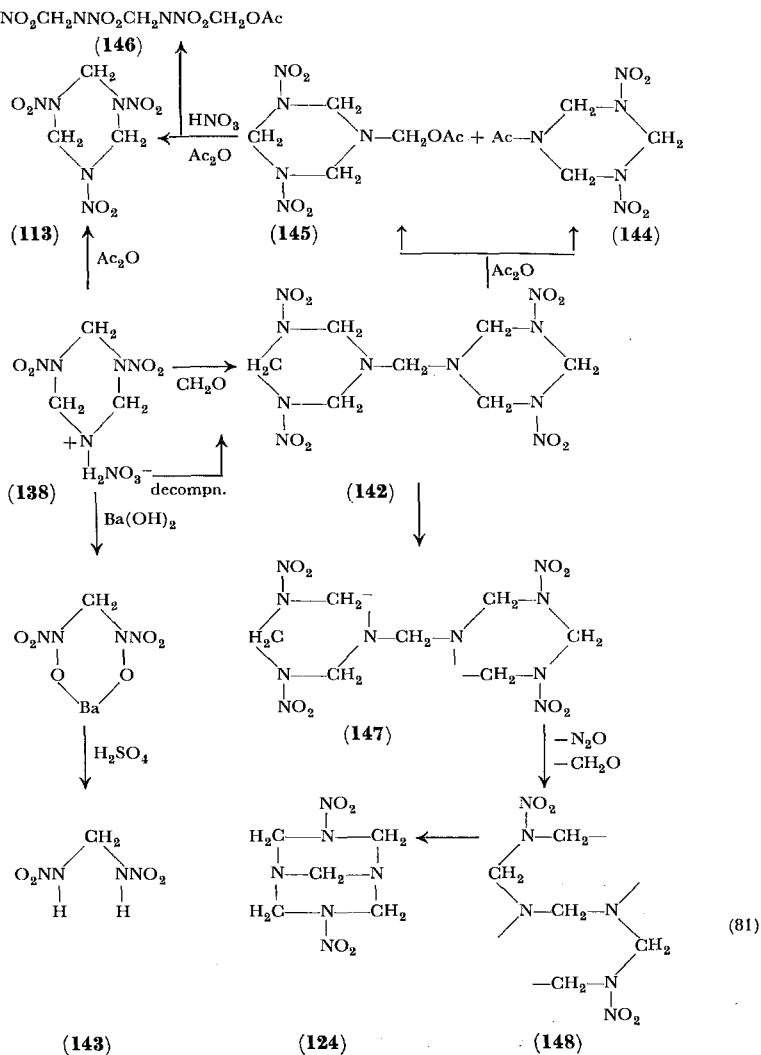


possible participation by **138**, was the discovery<sup>117</sup> in the precipitated gum of 3-nitramino-2-nitro-2-azapropylamine nitrate (**141**), which may be its decomposition product.

However, the reactions of **138**, are indirectly significant to the chemistry of the polymethylenenitramines. Although it seems not to participate in the formation of **113** from **125**, **138** can be converted to **113** by treatment with acetic anhydride (equation 81). This conversion is not unexpected since it ought to be a salt of a weak amine. As the free amine it is unstable and it decomposes to give formaldehyde and **141** which reacts with unchanged **138**, to form methylene-*bis*-1-[3,5-dinitro-1,3,5-triazacyclohexane] (**142**). Also it decomposes in

alkaline solution to give a (barium) salt which is that of dinitroaminomethane (**143**).

Although **142** is also an artifact not found in the nitration system its reactions contribute to a knowledge of the reaction mechanism. Treatment with acetic anhydride yields 1-acetyl-3,5-dinitro-1,3,5-triazacyclohexane (**144**) and 3,5-dinitro-3,5-diazapiperidylmethyl acetate (**145**). Treatment of these compounds with nitric acid and acetic anhydride yields **113** and 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (**146**). As would be expected the same products are



obtained when **142** is treated with the same nitrating system, i.e. nitric acid and acetic anhydride.

Compound **142** undergoes an interesting transformation when it is melted. Gas is evolved which may initially have been 2 equivalents of the unknown methylenenitrimine (**112**) but which appears as nitrous oxide and formaldehyde. The melt resolidifies after gas evolution has ceased and the solid is **124**. This rearrangement has been depicted as fission of bonds *r* and *s* (equation 81). The intermediate **147** suffers loss of formaldehyde and nitrous oxide and the remainder, **148**, recycles to **124**. It is possible that some unimolecular decompositions of this type occur in the various nitration systems.

### ***B. Polynitrimines from Acetic Anhydride and Nitrates***

The Hale nitrolysis of hexamethylenetetramine (**125**) in absolute nitric acid is undesirable from three aspects. First it employs a large excess of an acid which is difficult to make, most of which has to be recovered as nitrogen oxides and resynthesized. Secondly as was mentioned before, the spent liquors must be re-worked at once as a matter of safety. Third and most significant, half of the methylene groups in **125** are lost in the process. In consequence the information from British Intelligence that the German made cyclonite (**113**) from acetic anhydride and ammonium nitrate induced Ross and Schiessler to devise the process using paraformaldehyde which turned out to be the German process devised by M. Eble. However, the yield was about the same on the methylene basis as that obtained by the Hale nitrolysis. Then the idea of a 'combination' process was conceived by Werner Bachmann<sup>118</sup> in which the Hale nitrolysis of **125** would occur first and the remaining methylene would be converted to **113** by the Ross-Schiessler route. This concept was faulty only to the extent that it included the mechanism involving methylenenitramine. In the practical sense it was successful and, indeed, was found after the cessation of hostilities to be identical with the Knöffler-Eble process<sup>113</sup> which had been devised in Germany before 1936\*.

Although the Bachmann-Knöffler-Eble process gave nearly twice the yield of **113** on the methylene basis than did the Hale nitrolysis it was very difficult to control. Three feed streams: acetic

\* Knöffler originally introduced a variation of the Hale process in which ammonium nitrate was included with the nitric acid and **125**. Later these reagents plus acetic anhydride were combined to the Knöffler-Eble process.

anhydride, **125** in acetic acid, and ammonium nitrate in nitric acid had to be proportioned closely in order to obtain a maximum of **113** and a minimum of byproducts. The reasons for this control were not understood until it became apparent that the actual resynthesis step in the Bachmann-Knöffler-Eble process (and the synthesis step in the Ross-Schiessler process!) is the synthesis of **125** from formaldehyde and ammonium nitrate.

Although several studies<sup>119-121</sup> have been made of the conversion of ammonia and formaldehyde to **125** it was not known that the synthesis would occur in acidic media until the work of Baur and Ruetschi<sup>122</sup>. Acting on this information Winkler and coworkers<sup>123</sup> found that it is formed from paraformaldehyde and ammonium nitrate in acetic acid. Unfortunately for unequivocal proof the observation cannot be extended to a medium containing acetic anhydride because **125** reacts with it. However, a study of the byproducts of the reaction shows that they must have been formed from **125**.

The proportionate feeds of the reaction must be adjusted so that acetolysis and acetylation are minimal and nitrolysis is maximal. If too much acetic anhydride is present formaldehyde is converted to methylene diacetate which is ineffective toward regeneration of **125**. In like manner each hydroxymethyl terminus formed from nitrolysis must be made to demethylolate before it can acetylate; otherwise that fragment is fixed as a valueless byproduct. The demethylolation is favored at about 90° at which the acetic acid medium is maintained. If the reaction temperature is lower and if the concentration of acetic anhydride is high the amounts of byproduct increase at the expense of **113** yield. The reaction sequence is almost the same as that outlined for the Hale nitrolysis.

The desirable course of reaction commencing with the normal dinitrate salt of **125** involves first nitrolysis at *b*, *b'* leading to **127** (equation 82). Subsequent nitrolysis at *e* gives **113** and trimethylolamine. The latter seems not to be a building block for **125**<sup>121</sup> but it may be expected to demethylolate to suitable structural units. Significantly its trinitrate or triacetate has not been found among the byproducts.

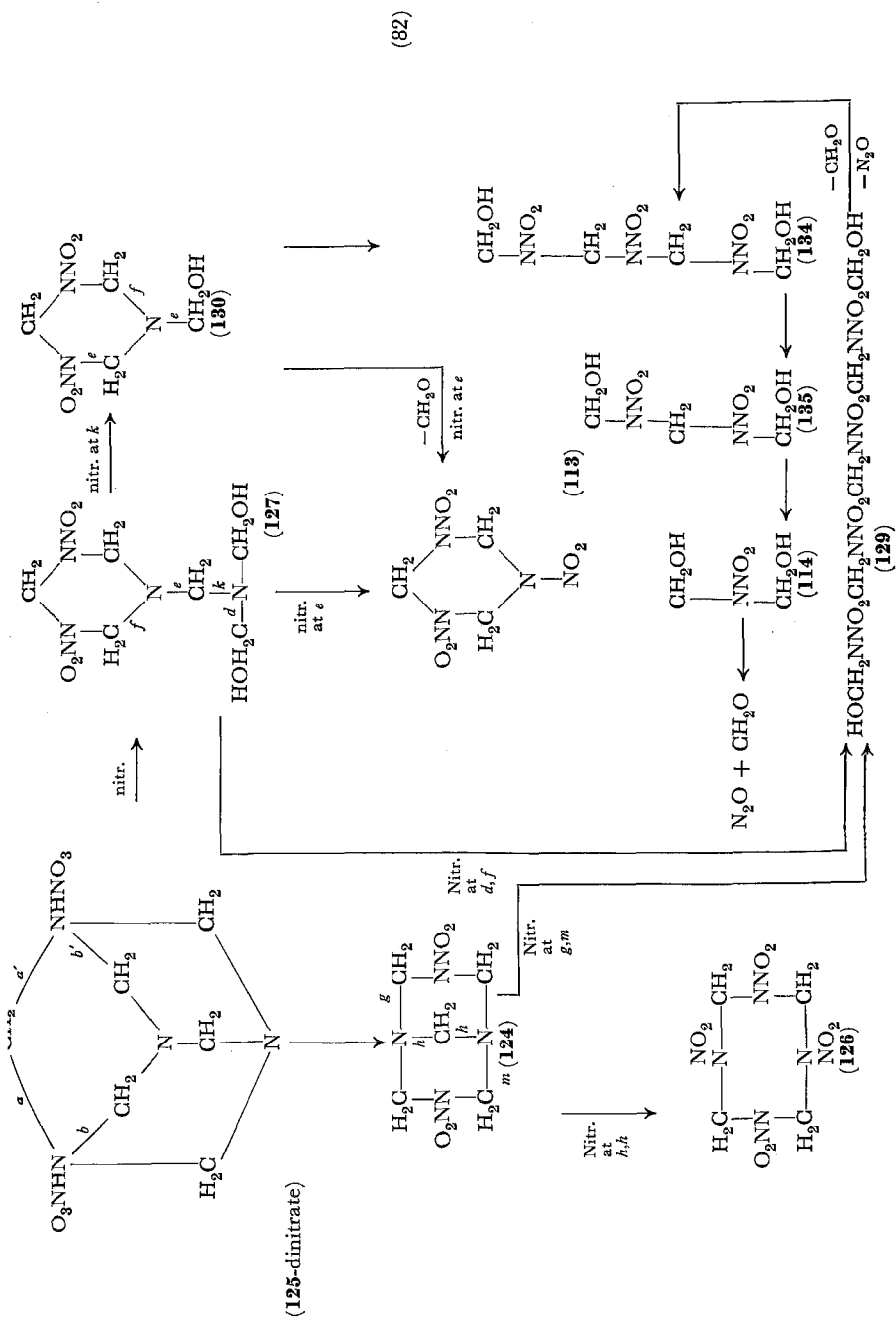
Unfortunately for a smooth reaction, nitrolysis alternative to that at *e* may occur, for instance at *k*. Besides the ubiquitous dimethanol-nitramine the product of low temperature nitration **130** will be formed. If ester formation (nitrate or acetate) does not occur it, too, will nitrolyze (or demethylolate and nitrate) to **113**. But if it does

esterify then nitrolysis at *f* may occur to give **134**. In a system rich in acetic anhydride this appears principally as the diacetate ester although it has also been detected as the mixed nitrate-acetate ester. If **134** is not esterified then it decomposes to formaldehyde and nitrous oxide *via* **135** and **114**. At any rate ring nitrolysis at *f* withdraws the methylene groups from direct conversion to **113**. Unless they are fixed by esterification these methylene groups appear as formaldehyde; thence by re-formation of **125** they go through the circuit again.\*

The conditions of nitrolysis are somewhat milder in acetic acid, by contrast to absolute nitric acid, even in consideration of a difference in temperature. The result seems to be the possibility of mononitrolysis at *a* followed by demethylolation at *a* and subsequent nitration. At least this is a reasonable sequence to explain that more of **124** is formed in the Bachmann-Knöffler-Eble process than in the Hale process. Further nitrolysis of this product at *h*, *h* leads to more of the contaminant **126** than is obtained by the Hale nitrolysis. Indeed when **126** is the desired product its yield may be increased by further amelioration of reaction conditions; this leads to more of the intermediate **124**. Of course some of **124** can nitrolyze at *g* and *m* and this may appear as the diacetate ester of 1,9-dihydroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (**129**). If it does not esterify then it joins the decomposition circuit back to formaldehyde. Incidentally the unravelling to give **129** can occur also by nitrolysis of **127** at *d* and *f*. If esterification occurs **129** will be isolable either as the diacetate or the mixed nitrate-acetate.

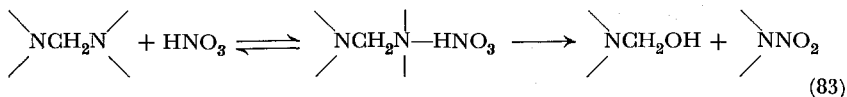
These nitrolyses have been described in terms of the mechanism involving nitronium hydroxide (see equation 77). The hydroxyl ion is a requirement of this mechanism but its presence in the anhydrous system presents a quandary. It would seem that the proposed mechanism is inapplicable in acetic anhydride and two alternatives are possible. The reaction of nitric acid and a methylenediamine proceeds molecularly and not ionically (equation 83). However, the

\* On the basis of tracer experiments by use of  $C^{14}$  and  $N^{15}$ , T. C. Castorina et al. (*J. Am. Chem. Soc.*, **82**, 1617 (1960) and *Ind. Eng. Chem. Prod. Res. Develop.*, **4**, 170 (1965)) have suggested, instead of the nitrolysis and resynthesis postulated above, that **125** and **124** undergo non-selective degradation to fragments such as  $HOCH_2NHNO_2$ , which then re-assemble to **113** and **126**. Although the conditions of their reactions and their yield calculations make direct comparison with the Bachmann-Knöffler-Eble process difficult it would appear that their results are not contradictory to the nitrolysis-resynthesis postulation.

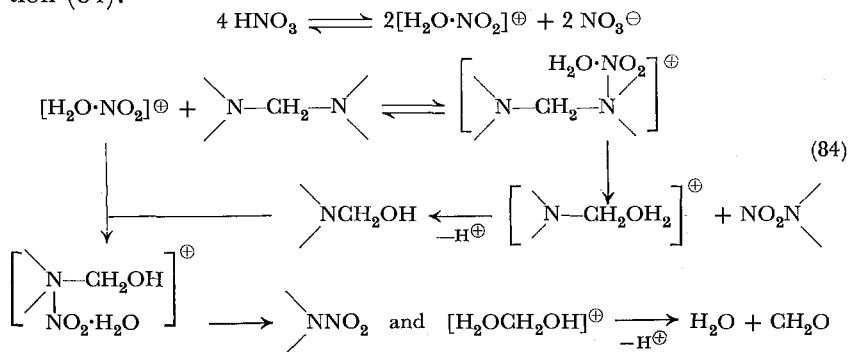




known chemistry of Mannich bases (of which **125** is one) favors



ionic rather than molecular reaction. In the more plausible (ionic) alternative the significant ion cannot be nitronium but rather is nitracidium ion. Without specifying the exact structure of the hydrated nitronium ion the nitrolysis may be depicted as in equation (84).

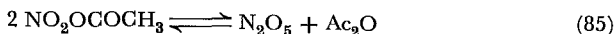


This mechanism conforms with the facts of the reactions leading directly to **113**. It is neither necessary nor especially plausible for the reaction leading to the linear polymethylenenitrimine diester by-products. These may be explained adequately by the nitronium ion mechanism (see equation 77).

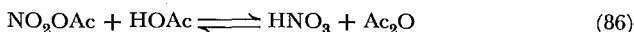
In fact there is evidence to support involvement of either a molecular nitrating species or else nitronium ion in certain steps of the overall synthesis. For example methylene-*bis*-dinitrodiazacyclohexane (**142**) reacts with benzoyl nitrate<sup>124</sup> in dry acetone to yield **113**. Although acetyl nitrate does not react with **125** in chloroform solution it does react in acetic acid. The recognizable product when 2 equivalents of acetyl nitrate are used is **124** while the product from almost four equivalents of acetyl nitrate is 1,9-diacetoxymethyl-4-aceto-2,6,8-trinitro-2,4,6,8-tetrazanonane, **149**<sup>125</sup> (equation 87). This substance may be obtained also by use of nitric acid and acetic anhydride at 40° and it will be discussed later. In the present instance it would appear that nitrolysis occurs in presence of acetyl and benzoyl nitrates, which may react either molecularly (as nitryl esters) or else as nitronium salts (ions or ion pairs). In either event the products will be esters such as **149**. It is tempting to consider that

nitracidium ion leads to the hydroxymethyl-terminated byproducts, while nitronium ion leads to their esters. The expectation that in the systems containing much acetic acid there is more nitracidium salt than nitronium salt supports such a speculation, because ester formation is ordinarily minimal in the synthesis of **113** from **125** where much acetic acid is present.

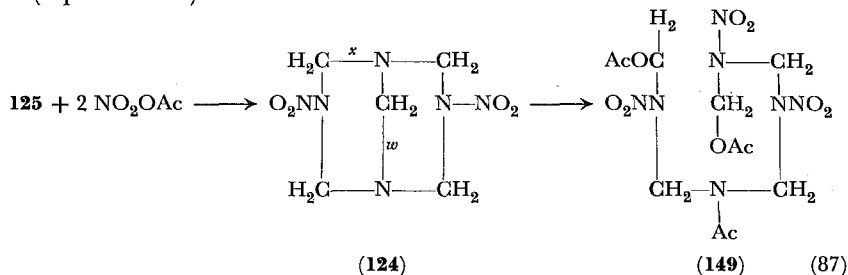
However, if one postulates nitronium ions one must also postulate acetonium ions in these acetic anhydride systems. For example the formation of **149** from **124** would seem to require a simple equilibration of acetyl nitrate (equation 85);



or else reaction of acetyl nitrate with acetic acid (equation 86)

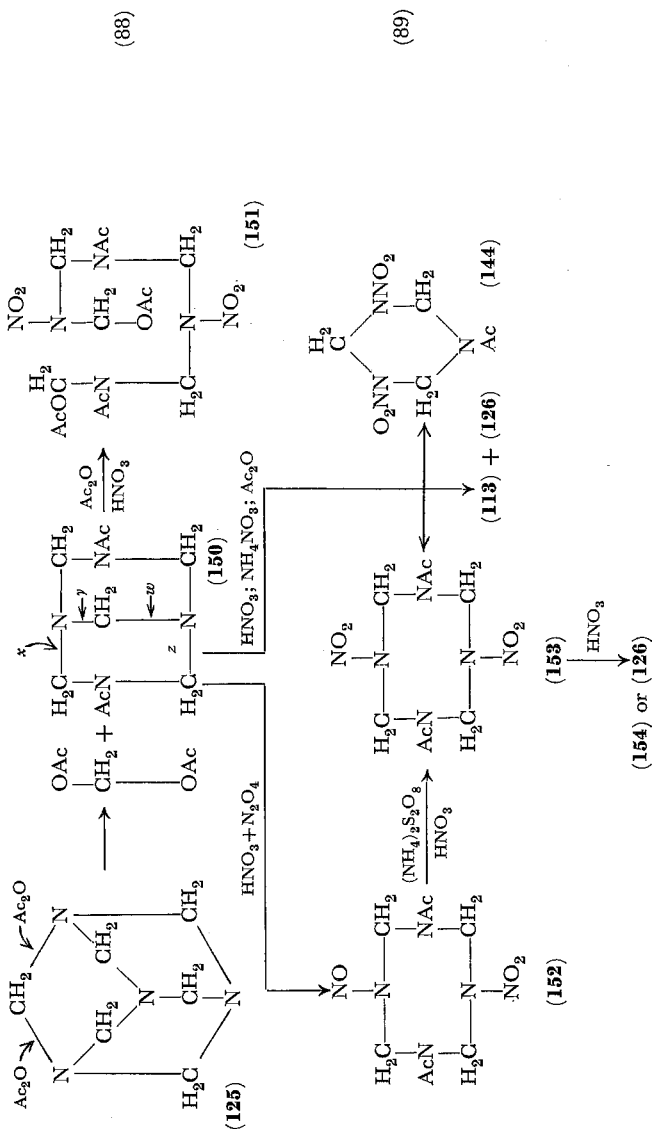


to give acetolysis ( $\text{Ac}\cdots\text{OAc}$ ) at  $w$  and nitrolysis ( $\text{NO}_2\cdots\text{OAc}$ ) at  $x$  (equation 87).



The acetolysis with acetic anhydride has already been mentioned in the conversion of **142** to the acetate ester **145** and **144** (equation 81). Indeed **125** itself was shown long ago<sup>126</sup> to undergo acetolysis to 1,5-endomethylene-3,7-diaceto-1,3,5,7-tetrazacyclooctane (**150**).

Compound **150** has not been treated with acetyl nitrate, but with acetic anhydride and nitric acid it undergoes only nitrolysis, first at  $w$  in the methylene bridge and then at  $x$  to give 1,9-diacetoxy-2,6-diacetyl-4,8-dinitro-2,4,6,8-tetrazanonane (**151**) (equation 88). The structure assumed for **151** depends, unlike the other tetrazanonanes in the series, on which of the linkages of the parent bicyclotetrazanonane is first solvolyzed. However, according to experience it is always the bond in the methylene bridge which first is broken. One of these experiences is exemplified by the reaction of nitric acid and dinitrogen tetroxide with **150**<sup>126</sup> where the entire methylene is removed. The structure of this nitroso-nitro derivative **152**, is simply



proven by persulfate oxidation<sup>127</sup> to 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazacycloöctane (**153**), which in turn in absolute nitric acid becomes either 1-acetyl-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane (**154**) or **126**, depending on the temperature of the reaction (equation 89).

It will be recalled that acetolysis of **125** leads to **150**. If this substance is treated under conditions of the Bachmann-Knöffler-Eble reaction with nitric acid, ammonium nitrate and acetic anhydride then besides **113** and **126** one may isolate small yields of **153** and **144** by nitrolysis of **150** at *w*, *y*, *x*, and *z*, respectively (equations 88–89). It may be presumed that the presence of **144** in Bachmann-Knöffler-Eble reaction systems arises from the acetolysis product **150** of **125**. No doubt **144** would be more prevalent in these systems were it not for its conversion by nitric acid to **113**. For the same reason **153** is not found because likely it is converted to **154** or **126**.

As has been shown above, certain polymethylenenitrimines can be formed from **125** by several reaction paths. Likewise some acetyl analogues can arise by processes other than acetolysis. This is the case for **154**, which seems to be formed from 1-acetamidomethyl-hexamethylenetetramine nitrate (**155**)<sup>128</sup>; at least conditions propitious for its formation are those which yield **154** (equation 90).

Inspection of formula **155** shows that acetamide must have been involved in its synthesis. In order to ascertain whether acetamide could be formed in the Bachmann-Knöffler-Eble system ammonium acetate was treated with **125** in acetic anhydride to give an 83 % yield. Also ammonium nitrate reacted with acetic anhydride but this reaction was much slower and the yield (7 %) was low. When either of these reaction systems included nitric acid no acetamide was formed. Therefore the formation of **155**, ought to be favored by a high ratio of ammonium nitrate and acetic anhydride to nitric acid in the Bachmann-Knöffler-Eble reaction system.

Actually **155** may be prepared under such conditions. Good yields are obtained when **125** mononitrate, acetamide and para-formaldehyde react in acetic acid, and combinations involving ammonium nitrate and acetic anhydride are also effective<sup>129</sup>. The structure as a quaternary salt has been amply demonstrated, finally by the inactivity of the salt towards diazomethane.

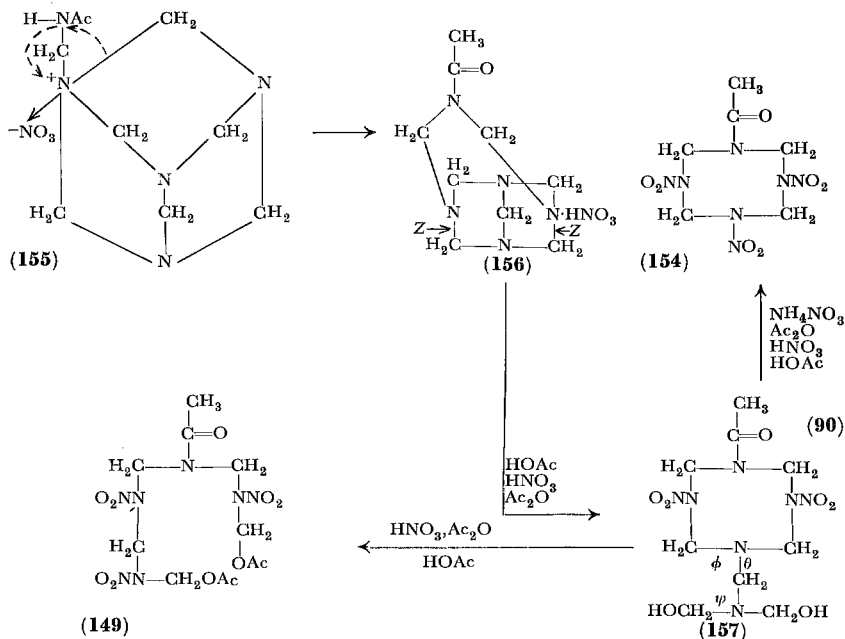
There is good evidence that this quaternary salt is the progenitor of **154**. Since formation of the quaternary salt is inhibited by nitric acid and yet requires this acid for conversion to **154**, there must be an optimum amount of nitric acid for highest yield. This has been

found to be the case. The yield of **154** also is enhanced by additional acetamide in the system. Finally when propionamide is added to the system comprised of acetic acid, its anhydride, ammonium nitrate and nitric acid together with **125** (the Bachmann-Knöffler-Eble reagents), the product is 1-propionyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, instead of the acetyl homologue **154**.

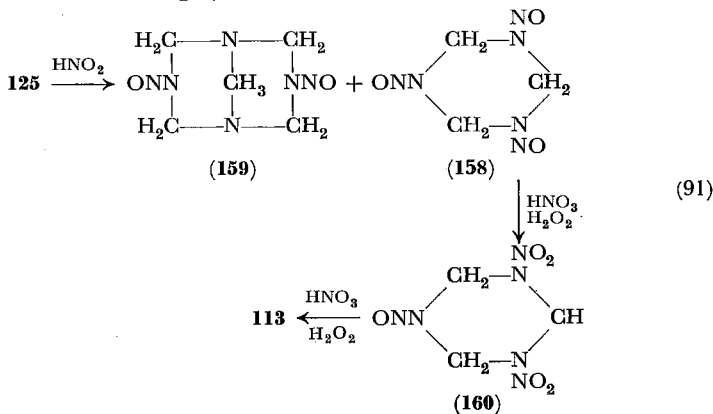
The case for acetamide involvement in the function of acetyl or propionyltrinitrotetrazacyclooctane is thus well-founded but the mode of transformation is not readily apparent. One may speculate that an uncommon rearrangement occurs. If the quaternary salt undergoes rearrangement to 1,5-endomethylene-3,7-endo-[2'-aceto-2'-aza-1,3-propylidene]-1,3,5,7-tetrazacyclooctane mononitrate(**156**) then nitrolysis at  $z$ ,  $z$  leads to 1-dimethanolaminomethyl-5-acetyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane (**157**) (equation 90). If ammonium nitrate is included with the nitric acid, acetic acid and its anhydride then terminal esterification is prevented and the dimethanolaminomethyl group is demethylolated and deaminated. The final result is nitrolysis at  $\theta$  with formation of **154**. In absence of ammonium nitrate esterification occurs followed by nitrolysis at  $\psi$  and at  $\phi$ , leading to a good yield of **149**, and a fair yield of dimethanolnitramine diacetate (**117**). It will be recalled that **149**, which here has been produced as a consequence of acetamide formation also has been obtained by acetolysis and nitrolysis of **124** by use of acetyl nitrate. Thus, as might be expected in this polymethylenenitrimine chemistry a single product may be formed by several distinct paths. Yet certain substances are conspicuously absent; for example, **124** cannot be found when **155** is treated with the Bachmann-Knöffler-Eble reagents. Conversely a detectable amount of **153** cannot be found when **150** is treated with the same reagents. It is the fact that the mechanism of reaction is best ascertained by a careful search for the substance that could not be formed from the chosen mechanism.

There are several methods for preparation of **113** free from any of the byproducts that have been mentioned above. The first of these involves oxidation of 1,3,5-trinitroso-1,3,5-triazacyclohexane (**158**). This substance is obtained, usually together with 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetrazacyclooctane (**159**) by treatment of hexamethylenetetramine with nitrous acid (equation 91).

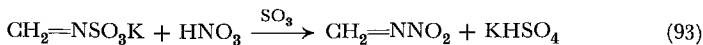
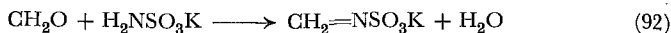
When **158** is freed from its impurity it may be converted to very pure **113** by adding it to a nitric acid-hydrogen peroxide system at  $-40^\circ$  (inflames at higher temperatures) and allowing the solution



to warm to room temperature. Of interest is the fact that if the reaction system is quenched by pouring it at  $-40^\circ$  onto ice the product is entirely 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (**160**). It would seem that reaction at only two of the three nitrogen atoms in the triazacyclohexane ring is characteristic whether nitrolysis of **125** or nitroso oxidation is involved. As might be expected the reactivity is a matter of degree, and **160** may easily be converted to **113** by the identical oxidizing system.

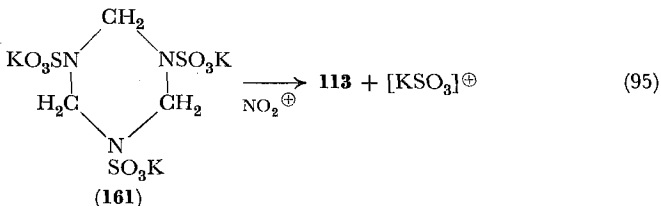


The second process for **113** without byproducts is named after Wolfram, its inventor. Equations 92–94 have been suggested as representative of the process<sup>109</sup>. Potassium methylene sulfamate, a



common chemical, is treated with absolute nitric acid in inhibitor-stabilized liquid sulfur trioxide, presumably to form methylenenitrimine. The yield and quality of the cyclonite supposedly formed by cyclotrimerization is excellent. Limitations of the process are availability of the sulfur trioxide monomer, control of its reaction with absolute nitric acid, and disposal as fertilizer of the potassium acid sulfate in the waste liquors.

In view of evidence cited above against methylenenitrimine as an intermediate, the reaction has been reinvestigated<sup>130</sup>. It has been found by molecular weight determinations that the salt called potassium methylene sulfamate actually is tripotassium 1,3,5-triazacyclohexane-1,3,5-trisulfonate (**161**). Therefore **113** is probably formed by exchange of potassiosulfonyl cation by nitronium ion on the preformed triazacyclohexane ring (equation 95). Incidentally the use of phosphorus pentoxide instead of sulfur trioxide provides



a much more workable process because its admixture with nitric acid is less violent than that with sulfur trioxide. Moreover **113** is stable in phosphoric acid but not in sulfuric acid, and either of these acids may be present if water is not excluded rigorously.

## X. PHYSICAL PROPERTIES OF NITRAMINES

### A. Vibrational Spectra

Raman studies account for the earliest vibrational spectra of nitramines. Frequencies were assigned<sup>131</sup> for the  $\text{NNO}_2$  group in *N*-methylphenylnitramine. Later methylnitramine (molten) and its ammonium salt (solid) were examined<sup>132</sup> by Wittek who concluded

from similarities between the two that the isonitramine structure was predominant. In the same year from a crystal of **113** assignments<sup>133</sup> were made for deformation ( $676\text{ cm}^{-1}$ ), symmetrical stretch ( $1212\text{ cm}^{-1}$ ), and antisymmetric stretch ( $1572\text{--}96\text{ cm}^{-1}$ ).

In 1948 Kohlrausch and Wittek presented a more complete study of primary nitramines and their salts, also of secondary nitramines as well as nitrourethanes and their salts. From a comparison of these results Wittek's opinion was revised against the isonitramine structure for primary nitramines.

The Raman spectrum of nitramine itself was described in the latter paper but a more elaborate report of nitramine and its methyl derivatives appeared later<sup>134</sup> together with the corresponding infrared data. An abbreviated comparison of the two spectral types is shown for nitramine in Table 2. Assignments have been facilitated by use of deuterio-nitramine. Similar spectra and assignments were made for methyl and dimethylnitramine. It was concluded that these substances were molecularly planar due to *p*-orbital overlap.

Several studies confined to infrared measurements have been made for purposes of characterization and group identification. Some of the secondary aromatic nitramines were examined<sup>135</sup> and 19 nitramide and nitramidine types were studied in detail<sup>136</sup> to show the variance in the principal  $\text{NO}_2$  bands at  $1500\text{--}1600$  and  $1200\text{--}1300\text{ cm}^{-1}$ . Also the spectra of 10 aliphatic secondary nitramines have been reported<sup>137</sup> without spectra assignments.

An attempt has been made to distinguish nitramines and the isomeric nitrimines by infrared spectroscopy<sup>138</sup> but in one instance the assignment of the nitrimine structure does not seem to correlate with studies using diazomethane<sup>31</sup> which seem to show that the nitration product of 2-aminothiazole (7) is the nitramine, 8.

The importance of infrared spectroscopy as an analytical method for nitramines is obvious because their explosive properties render melting points and thermal analyses undesirable criteria, especially for production control. Moreover many nitramines decompose at their melting points, especially at elevated temperatures. HMX, (**126**) is such a substance (m.p.  $278^\circ$ , decomp.) the presence and amount of which must be known when it occurs as an impurity in commercial **113**.

The analysis for **126** in **113** involves the crystalline mixture in nujol mulls or potassium bromide wafers. In common with many nitro compounds there are at least four crystalline forms of **126**.



TABLE 2. Raman and infrared spectra of nitramine from thin films,  $\text{cm}^{-1}$ .

Raman	3278	1642	1547	1370	1305	1176	1050	716	598				
IR	3287	3085	2700	1760	1613	1546 1534	1379	1257	1175	1043	783	709	596
Assignment	NH <sub>2</sub> ν sym	2 × 1540	3287 minus 596	1176 plus 596	NH <sub>2</sub> δ s	NO <sub>2</sub> ν asym vs	NO <sub>2</sub> ν sym	716 plus 596	NH <sub>2</sub> or 2 × 596	N—N ν plane	NNO <sub>2</sub> out of plane rock	PNP δ	N—NO <sub>2</sub> in-plane deformation

Ordinarily this multiplicity would not be troublesome because the IR spectra of polymorphs resemble one and another closely<sup>139</sup>. However, the several crystalline forms of **126** gave spectra so distinctive that they could not be classified as simple polymorphs.

## B. Ultraviolet Spectra

The introduction of ultraviolet spectroscopy overlapped the period of popularity which nitramine chemistry enjoyed at the beginning of the century. Consequently as early as 1908 ultraviolet and visible spectra of nitramine and substituted nitramines were reported in the literature. The extent of these reports and the usefulness for analytical purposes prompts a separate bibliography as follows:

Nitramines, Ultraviolet (1908)<sup>140</sup>.

*N*-4-dimethyl-2,6-dinitrophenylnitramine, Visible (1911)<sup>141</sup>.

*N*-4-dimethyl-2,6-dinitrophenylnitramine, Ultraviolet (1912)<sup>142</sup>.

Picrylmethylnitramine (Tetryl), Ultraviolet (1913)<sup>143</sup>.

Copper salts of methyl- and ethylnitramine, Ultraviolet (1913)<sup>144</sup>.

Nitroguanidine and aminonitroguanidine, Ultraviolet (1929)<sup>145</sup>.

Nitramine, methylnitramine, and dimethylnitramine, Ultraviolet (1940)<sup>146</sup>.

*N*-methyl-2,4-dinitrophenylnitramine, Ultraviolet (1948)<sup>148</sup>.

Primary and secondary nitramines and nitramides, Ultraviolet (1948)<sup>76</sup>.

All types, prime reference, Ultraviolet (1949)<sup>149</sup>.

Trishydroxymethylnitramine and its salts, Ultraviolet (1949)<sup>150</sup>.

Nitramines, nitrocarbarnates, and salts, Ultraviolet (1951)<sup>151</sup>.

Linear and cyclic nitramidines, Ultraviolet (1951)<sup>152</sup>.

5-Nitraminotetrazoles and their salts, Ultraviolet (1951)<sup>153</sup>.

Primary nitramines and polynitrimines, Ultraviolet (1951)<sup>154</sup>.

Polynitrimines, Ultraviolet (1952)<sup>155</sup>.

Nitroguanylhyazones of aldehydes, Ultraviolet (1952)<sup>156</sup>.

Nitramidines, Ultraviolet (1953)<sup>157</sup>.

These studies seem to have been made purely for purposes of product identification. Essentially no interpretation of the electronic spectra have been made.

### C. X-Ray Diffraction

Besides the ones mentioned on page 619, there have been several single-crystal studies reported. In 1947 Costain and Cox<sup>158</sup> made a partial study of dimethylnitramine, from which they concluded that the molecule was a planar resonance hybrid with appreciable nitrogen-nitrogen double bond character. Later the parameters of nitramine were measured<sup>159</sup>.

The nitrimino structure for nitroguanidine has been confirmed by a single-crystal study<sup>160</sup>. A polynitrimine, HMX has also been examined<sup>161</sup>. Structural analysis of several of the crystalline modifications has confirmed the suspicion raised by infrared studies that these modifications involve conformational differences rather than simple polymorphism.

An attempt has been made to determine the structure of *N,N'*-dinitropiperazine but the facilities for calculation available at the time were inadequate for a complete determination because of an apparent asymmetry<sup>162</sup> of the molecule<sup>137</sup>.

The small amount of sample required for X-ray diffraction of powders makes characterization even safer than does infrared spectral analysis. Moreover polymorphism is common among nitro compounds and the difference in spectra among true polymorphs is minimal. By contrast the X-ray powder diagrams are distinctive and have been recorded in a number of instances. Ethane-1,2-dinitramine, nitroguanidine, bis-nitroxyethylnitramine, cyclonite, HMX-I and 1-acetyl-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane have been characterized in this manner<sup>163</sup>. The powder diagrams of the crystalline modifications, HMX-I, II, III and IV have been determined (as well as an HMX-dimethylformamide 1:1 complex) for identification and for proof that there was no conversion of these 'polymorphs' from the less stable to the more stable during determinations of spectra and dielectric constant<sup>139</sup>. Actually most of the crystalline nitramines synthesized by G. F Wright and his co-workers have been characterized by powder diagrams.

### D. Nuclear Magnetic Resonance Spectra

Only one publication has appeared in which the *N*-nitro type of compound has been examined by NMR. This is a study of simple nitramine<sup>164</sup> and of nitrourethane. The authors conclude that the protons are of the amino type.

### E. Electrical Polarization

The assignment of the nitrimide structure for nitroguanidine by Kumler and Sah<sup>98</sup> and for nitriminoimidazolidine (**83**) and nitro-nitriminoimidazolidine (**94**) by Kumler<sup>100</sup> has already been mentioned. The remainder of electrical polarization studies may be found in a summary published about nitro compounds, in which nitramines and polynitrimines are discussed<sup>165</sup>. The N—NO<sub>2</sub> 'group moment' is large (4.4–4.6 D) despite the degeneracy that is apparent from other physical measurements. In consequence the measurement of dielectric constant can be precisely informative.

The electrical polarization of electron-nucleon reactance with the field may be measured by use of crystalline solids<sup>166,139</sup> because the crystal lattice restriction prevents a dipolar substance from orienting itself with respect to the electric field. If, then, a measurement is made of this substance in solution where total polarization ( $P_T$ ) is the sum of electron-nucleon ( $P_E + P_A$ ) and orientation ( $P_O$ ) polarization then the latter may be determined precisely according to equation (96).

$$P_O = P_T - (P_E + P_A) \quad (96)$$

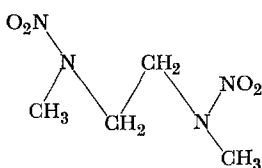
From this orientation polarization an evaluation of the dipole moment (from which  $P_O$  originated) can be made. According to Debye the moment,  $\mu$  in Debyes, is given by equation 97,

$$\mu = 0.012812 \times 10^{-18} \sqrt{P_O \text{ (abs temp)}} \quad (97)$$

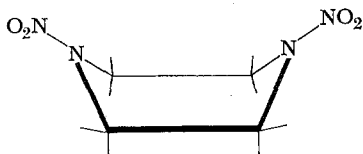
and is commonly thought to be in error only to the extent that the solvent is polarized by the solute dipole.

Characteristic parameters are listed for aliphatic nitramines in Table 3. The measured density is needed for calculation of  $R_D$  (electron polarization,  $P_E$ ) and  $P_{E+A}$  (electron-nucleon, distortion polarization) from the refractive index and dielectric constant, respectively.  $R_D$ -additive is calculated from Eisenlohr-atom<sup>167</sup> and Vogel-bond<sup>168</sup> values. By subtraction of  $R_D$  from  $P_T$  the moment may be calculated but it will be in error to the extent that atom polarization is not included in the refractive index measurement since  $R$  is determined in the electronic frequency range where the nucleons cannot follow the alternating field. These nucleon reactances (at infrared frequencies) are included with electron reactances ( $P_E + P_A$ ) at radio frequencies. Therefore the moment values in the last column of Table 3 are the more accurate, although when moments are large the difference is minimal.

The large moment of the nitramino group, exemplified by the first six items of Table 3 is a useful device for evaluating conformation in substances containing several of these groups. For example cyclonite oxide (**136**) cannot be planar else its moment would be about  $4.6 \text{ D} - 1.3 \text{ D} = 3.3 \text{ D}$  ( $2 \times 4.6 \cos 60^\circ - 2 \times 1.3 \cos 60^\circ$ ) instead of the  $5.64 \text{ D}$  observed. Likewise the moment of cyclonite would be zero, if planar, instead of  $5.78 \text{ D}$ . However, a more elaborate analysis of these conformations is inadvisable with the data available when the behavior of *N,N'*-dinitropiperazine is examined.



(163)



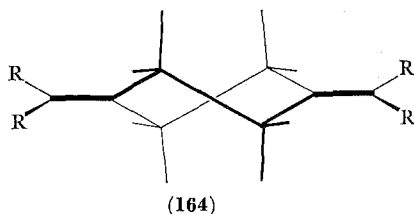
(162)

If this substance existed simply in a chair conformation its moment ought to be zero. In fact at  $20^\circ$  in dioxane solution a value of  $2.21 \text{ D}$  has been found. This moment also cannot be explained by assumption of the boat form **162** which would be expected to have a moment of about  $4.5 \text{ D}$ . Distortion of either chair or boat would result in a moment of intermediate value such as the  $3.52 \text{ D}$  found for *N*-methylnitramino-*bis*-ethane (**163**). However, the facts seem to show another complication in the variance of moment ( $2.21$ – $2.68 \text{ D}$ ) with respect to a temperature difference of  $20$ – $40^\circ$ . This variance is unexpected in terms of equation (97) since translational energy is presumed to be compensated by the temperature factor. In any case the higher the temperature the lower should be the polarization because thermal agitation ought to disorient the dipole, whereas the data in Table 3 show that the polarization of dinitropiperazine increases at higher temperatures.

Because of this abnormal behavior with respect to ambient temperatures it is assumed that the piperazine ring is neither boat nor chair. Instead it exists in a flexible conformation<sup>162</sup> in which the contributing isomers<sup>137</sup> may be summarized in terms of two extremes. The one of high moment is exemplified by the boat form **162**, and the other of low or zero moment, is shown as **164** ( $R = \text{oxygen atom}$ ) and has been called the extended form<sup>169</sup>.

TABLE 3. Physical properties of nitramines.

Substance and temp., °C	Electrical polarization in dioxane						
	$d_4^{20}$	$P_T$	$n_D^{20}$	$R_D$ Abbé	$R_D$ additive	$P_{E+A}$ pellets	$\mu(D)$
							$P_T - R_D$ $P_T - (P_E + P_A)$
Dimethylnitramine, 20		470			21.8		4.61
Di- <i>n</i> -propylnitramine, 20	0.995	517	1.4370	40.0	39.9		4.76
Diisopropylnitramine, 20	1.104	548			39.9	51.2	4.91
Di- <i>n</i> -butylnitramine, 20	0.962	538	1.4557	49.3	49.1		4.82
Nitromorpholine, 20	1.363	248			30.1	38.5	3.22
2-Cyanoethyl- <i>bis</i> -nitramine, 20	1.424	378			38.1	47.1	4.02
N-Methylnitramino- <i>bis</i> -ethane, 20	1.446	315			40.6	54.5	3.61
1,3-Dinitro-1,3-diaza-5-oxacyclohexane, 20	1.824	706			35.4	35.3	5.64
1,3,5-Trinitrotriazine, 20	1.78	751			43.7	47.0	5.79
N,N'-Dinitropiperazine, 20	1.638	145	1.617	38.6	38.4	42.1	2.21
Same, 25		154					2.33
Same, 30		165					2.46
Same, 40		183					2.68



Moreover this flexibility is assumed to correspond to a conformational frequency of which **164** is the unexcited and **162** is an excited species. This frequency would seem to be close to that of the ambient 'thermal' region where radiation is so intense that a portion of the molecules not much less than 50 % are excited at 20° and the population will increase if excitation frequency 'peaks' at a higher temperature. It is assumed that these induced dipoles will contribute to the observed moment.

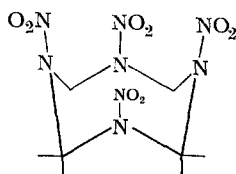
Ostensibly-centrosymmetric substances like benzoquinone<sup>170</sup> and diphenylmercury<sup>171</sup> which exhibit a temperature-variant dipole moment show strong absorptions at 117 and 100 cm<sup>-1</sup> respectively. In view of these absorptions in the 'thermal' range for condensed systems it is not unexpected to discover that *N,N'*-dinitropiperazine absorbs strongly at 123 and also at 102 cm<sup>-1</sup>.

Inspection of Table 3, Entries 3, 5, and 6 show that nitramines of high dipole moment are found to have distortion polarizations, ( $P_{E+A}$  measured in the solid state) which are 8–11 cc greater than the  $P_E$  ( $R_D$ ) calculated from atom<sup>167</sup> or bond polarizabilities.<sup>168</sup> The difference, attributable to reactance of nucleons in their electron matrix (so-called atom polarization,  $P_A$ ) indicates a relationship between this part of the distortion polarization and the orientation polarization of highly-polar substances.

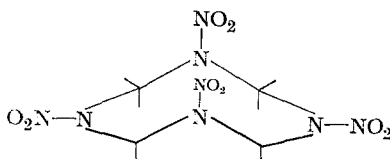
Table 3 shows that  $P_A$ , 13.9 cc for *N*-methylnitramino-*bis*-ethane (**163**) indicates some additivity of the polar effects. However,  $P_A$  for 1,3-dinitro-1,3-diaza-5-oxacyclohexane (**136**) is zero, while for cyclonite (**113**) and *N,N'*-dinitropiperazine it is relatively low (3.3–3.7 cc). From these values it is evident that the effect on  $P_A$  of polar groups is algebraically additive with consequent diminution of  $P_A$  when the groups are symmetrically opposed.

This property has been utilized in order to attempt an understanding of the difference between the crystalline forms (HMX-I, II, and III) of this polynitrimine. At 23° the differences between the calculated  $P_E$  ( $R_D$ ) of 58.3 cc and the  $P_{E+A}$  calculated from dielectric

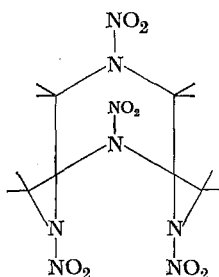
constants are 5.3, 28.7 and 21.2 cc, respectively. Assuming the concept of dipole apposition the following approximate conformations of HMX—II, HMX—III and HMX—I are suggested.



HMX—II( $P_A$ , 28.7 cc)



HMX—III( $P_A$ , 21.2 cc)



HMX—I( $P_A$ , 5.3 cc)

These conformational assignments alone do not explain the unusual spectra mentioned above because they could be a consequence of polymorphism, whereas the spectra indicate that other effects are involved. In order to rationalize the spectra and to decide whether polymorphism or another phenomenon is involved, the temperature coefficient of  $P_{E+A}$  was examined. Distortion polarization ought to be temperature-independent because the polar groups in the crystal are not disoriented by translational motion. Indeed Table 4 shows for the first 5 compounds (all with appreciable  $P_A$ ) that over a 68° temperature range  $P_{E+A}$  is constant within experimental error. Likewise HMX—I for which a highly symmetrical conformation has been chosen shows  $\Delta_{l(P_{E+A})}$  just outside experimental error. However, the variance for HMX—II and HMX—III (1.2–1.3 cc)



TABLE 4. Distortion polarization at  $+28^\circ$  ( $t_1$ ) versus that at  $-40^\circ$  ( $t_2$ ).

Substance	$t$ ( $^\circ\text{C}$ )	$\epsilon$	$d_4^{20}$	$P_D$ (cc)	$\Delta P_D$ ( $t_2 - t_1$ )
Anthraquinone	$t_1$	3.200	1.421	62.0	
	$t_2$	3.217		62.3	+0.3
Zirconium acetylacetonate	$t_1$	2.937	1.412	135.3	
	$t_2$	2.938		135.4	+0.1
Hexachlorobenzene	$t_1$	2.832	2.044	52.8	
	$t_2$	2.839		52.9	+0.1
Sodium chloride	$t_1$	6.125	2.165	17.1	
	$t_2$	5.944		16.8	-0.3
Potassium chloride	$t_1$	5.040	1.984	21.6	
	$t_2$	4.927		21.3	-0.3
HMX-I $P_A = 5.3$ cc at $23^\circ$	$t_1$	3.087	1.91	63.6	
	$t_2$	3.118		64.1	+0.5
HMX-II $P_A = 28.7$ cc at $23^\circ$	$t_1$	4.671	1.87	87.0	
	$t_2$	4.544		85.8	-1.2
HMX-III $P_A = 21.2$ cc at $23^\circ$	$t_1$	3.868	1.82	79.5	
	$t_2$	3.776		78.2	-1.3

indicate strongly that within the confines of the space that they occupy in their crystals they are undergoing conformational liberation of specific frequency which may be dependent on but not directly related to the lattice motion. The spectra in the  $100\text{ cm}^{-1}$  region are much more difficult to interpret than that for *NN'*-dinitropiperazine but they seem to indicate a similar behavior of dynamic conformation.

At the beginning of this chapter it was pointed out that nitramines were originally important substances for theoretical organic chemical studies. But such interests gradually decreased. Thereafter nitramines and their congeners received scant attention except when they were needed as military explosives. However, the recent developments in respect of their physical properties may once more make nitramines important for theoretical studies.

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# Author index

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## A

- Abe, T., 45, 46(139), 48(139), 75, 103, 105, 119(173), 130, 131, 377(166), 477, 307 (312,314-316), 521, 533(372), 558(314, 370), 560(315,316,368,369), 566 (372, 374), 567 (314,371-373), 575(314), 576 (314), 587(546), 606, 607, 611
- Abidova, M. F., 244(164), 292
- Abraham, R. J., 111(213), 132
- Abramovitch, R. A., 283(419), 298
- Abrazhamova, E. A., 235(111), 290
- Abshire, C. J., 243(156), 264(304), 292, 296
- Achmatowicz, B., 411(350), 482
- Adams, M. L., 492(277), 605
- Adams, N. G., 213
- Adams, R. N., 37(121), 38(121), 62(121), 63, 74, 76, 121(302), 124(314), 134, 135, 223(43), 288
- Addison, L. M., 302(8,14), 343
- Adeniran, M. A., 491(29), 516(29), 517 (29), 541(29), 545(29), 549(29), 550(29), 598
- Adhikary, P., 380(191), 414(191), 418-420 (191), 422(191), 423(191), 447(191), 478
- Aditya, S., 105(164), 130
- Adolph, H. G., 89(56), 90(56), 127, 366 (118), 373(118), 374(118,148a), 375(118), 376(118), 476, 477
- Ahlers, K. D., 277 (387), 298
- Ahlers, W. C., 120(290), 134
- Ahmad, M., 86(32), 126, 270(335), 296
- Ainscough, J. B., 377(171), 477, 520(352-354), 521, 558(353), 606, 607
- Akamatu, K., 119(276), 133
- Akashi, K., 469(483), 486
- Akatsuka, M., 560(442-445), 576(518), 609, 611
- Akermark, B., 116(259), 133
- Akhmedzade, D. A., 228(65), 289
- Akhtar, M., 222(35), 288
- Akiyoshi, S., 280(409), 281(409), 298
- Albrecht, H., 328(143), 346, 352(16), 353(16), 473
- Aleksandrova, A. M., 491(262), 505(262), 604
- Alessandri, L., 268(325,329), 275(369), 287(437), 296, 297, 299
- Alet, I. R., 495(286), 508-510(286), 549 (286), 605
- Alexander, L. G., 302(7), 342
- Alexéeff, P., 390(260), 480
- Allen, C. F. H., 499(290), 605
- Allen, C. R., 520(361), 558(361), 577(361), 607
- Allen, J. D., 367(135), 476
- Allen, J. G., 496(285), 497(285), 500(285), 508(285), 605
- Allendoerfer, R. D., 62(193), 76, 124(327), 135
- Allentoff, N., 618(26), 620(26), 681
- Alt, L. L., 407(341), 482
- Altieri, L., 491(49), 498(49), 502(49), 514 (49), 534(49), 535(49), 537(49), 540(49), 550(49), 599
- Altschuler, S., 90(74), 111(228), 128, 132
- Aluchna, G., 468(479), 469(479), 486
- Amarosa, M., 278(392), 279(392,396), 298
- Ambühl, G., 397(290), 481
- Amis, E. S., 554(408), 557(408), 608
- Anagnostopoulos, C. E., 323, 346
- Anderson, D. H., 407(341), 482
- Anderson, G. J., 334(170), 347
- Anderson, J. K., 109(204), 132
- Anderson, K., 207(137), 212
- Anderson, R. S., 311, 344

Andreades, S., 221(30), 288  
 Andreasch, R., 412(364), 482  
 Andreeva, L. M., 328 (141), 333(141), 346  
 Andrew, L. W., 380(190), 478  
 Andrews, L. J., 116, 117(268), 119(268),  
 120(268,278), 133, 134, 520(355), 607  
 Angeli, A., 233(96), 237(121), 264(299),  
 280(406,407), 290, 291, 295, 298, 614(13),  
 628, 645, 648, 681  
 Angelico, F., 233(95), 237(121), 264(299),  
 280(406), 290, 291, 295, 298  
 Anger, V., 280(403), 298  
 Ans, J. D., 308(36), 343  
 Antony, A. A., 116(258), 133  
 Aoyama, Y., 245(170), 292  
 Aplin, R., 181(58), 210  
 Applegate, V. C., 102(111), 129  
 Arai, H., 377(166), 477, 521(373), 567  
 (373), 607  
 Arbuzov, Yu. A., 270(337), 296  
 Archibald, T. G., 431(444a), 485  
 Arendt, V., 247(186), 292  
 Arens, A., 407(342), 482  
 Aristoff, E., 667(129), 684  
 Arizan, S., 102(136), 130  
 Armand, J., 240(131), 291, 353(44-48),  
 354(44,47), 358, 366(47), 373(47), 374  
 (47), 383(47), 385(46,47), 386(46,47),  
 387(47), 388(47,179), 389(47), 395(47),  
 398(44), 400, 404(321), 438(47), 439(47),  
 472(44,47,321), 474, 478, 481  
 Armarego, W. L. F., 383(217), 479  
 Arnaud, P., 94, 128  
 Arndt, F., 417-419(394), 420(394,412),  
 422(394,412), 423(394), 424(394), 438  
 (394), 442(394), 443, 446(394), 451(394),  
 452(394), 459(394), 483, 484  
 Arnold, A. P., 364(110), 368(110), 472  
 (110), 476  
 Arnold, C., Jr., 219(17), 288  
 Arnold, H., 327(138), 346  
 Artem'ev, A. A., 399(302), 481  
 Arth, G. E., 37(120), 74, 305(28), 307(28),  
 343  
 Arumugam, N., 322(110), 345  
 Astle, M. J., 364(110), 368(110), 472(110),  
 476  
 Aston, J. G., 260(252), 294

Atkins, P. W., 32(100), 74  
 Aue, W., 244(168), 292, 555(415), 608  
 Auwers, K. v., 417(395), 419(395), 422  
 (395), 452(452), 483, 485  
 Ayer, D., 192, 211  
 Ayscough, P. B., 123(313), 135, 191, 211

## B

Babers, F. H., 310(48), 344  
 Babievskii, K. K., 340(184), 348, 378(178),  
 380(178), 383(178), 397(288,289), 436  
 (178), 478, 480, 481  
 Babo, H. V., 621(32), 622(32), 642(32), 681  
 Bacarella, A. L., 284(425), 299  
 Bachman, G. B., 302, 314(61), 316(82),  
 318(82), 343-345, 451(451), 485  
 Bachmann, W. E., 640(97), 660, 667(127,  
 128), 683  
 Backer, H. J., 590, 611, 614, 624(9), 673  
 (143,144), 681, 684  
 Baer, H. H., 411(349, 350), 482  
 Baeeyer, A., 223(42), 288  
 Bagratishvili, G. D., 115(251), 133  
 Bailey, A. S., 564(469), 565(469), 609  
 Bailey, P. S., 243(156), 264(304), 292, 296  
 Bailey, S. D., 125(337), 135  
 Baird, J. C., 15(35), 17-19(35), 23(71),  
 32(71,99,101), 68(35), 72-74  
 Baitinger, W. F., 112(229), 114(229), 132  
 Bak, B., 106, 131  
 Baker, A. W., 143(21), 162  
 Baker, J. W., 549(397), 608  
 Baker, M. S., 333(162), 347  
 Baker, T. N., III, 231(84), 290  
 Bakin, M. A., 399(303), 481  
 Balasubramanian, A., 93, 94(87), 100(100),  
 103, 113, 115(255), 128-130, 133  
 Balch, A. L., 124(322a), 135  
 Baldeschwieler, J. D., 57(167), 75  
 Baldock, H., 319(96), 345  
 Baldwin, J., 207(139), 212, 259(245), 294  
 Baliah, V., 505(309), 520(365), 558(309,  
 365), 571(365), 575(365), 577(365), 605,  
 607  
 Ballio, A., 251(211), 293  
 Baltazzi, E., 151(53), 163  
 Baly, E. C. C., 673(140), 684

- Bambenek, M. A., 124(322a), 135
- Bamberger, E., 186(78,79), 188, 206(134), 210, 212, 240(134,138), 241(139,140,144,145), 242(144,146,152), 245(173), 249 (195), 251(206), 260(257), 264(297), 269 (332), 271(348,349), 272(348,349,352,354), 282(413,416), 283(349), 285, 291–299, 306(31), 343, 350, 351, 359(83), 378 (83,180), 380(83,180), 389(244), 390(252), 395, 397(6,292–299), 398(6,295–299), 400 (296), 401, 419(297), 420(6,298,299), 421 (295), 424, 444(298), 447(298,299), 473, 475, 478, 479, 481, 614, 616, 617(18), 619, 621(32), 622(18,32,36–38), 623(18,37), 633, 638(37), 642(32), 680–682
- Bamkole, T. O., 490(30), 497(30), 501(30), 504(30), 529(30), 545(30), 546(30), 552 (30), 578(30), 599
- Bankert, R. A., 333(159), 347
- Banks, R. E., 222(38), 269(331), 288, 296
- Banthorpe, D., 172(31), 209
- Banus, J., 274(365,366), 297
- Barcellona, S., 251(211), 293
- Barltrop, J. A., 213
- Barnes, L., 111(223), 132
- Barnett, R. T. F., 673(142), 684
- Barr, D. A., 266(320), 296
- Barr, E. W., 510(321), 524(321), 606
- Barrett, G. R., 430(441), 431(441), 433 (437), 434(441), 435(437), 484, 485
- Barrett, H. S. B., 568(482), 610
- Barrick, P. L., 319(97), 345
- Barry, J. E., 491(109), 503(109), 524(109), 525(109), 600
- Bartkus, E. A., 594, 612
- Bartolotti, L., 569(494), 571(494), 576 (494), 610
- Barton, D. H. R., 221(34), 288, 323(119), 346
- Barton, S. S., 625(51), 682
- Bartusch, G., 254(228), 279(397), 294, 298
- Basco, N., 219(20), 285(432), 288, 299
- Baskov, Y. V., 90(73), 107(185), 128, 131, 362(91), 475
- Bassett, J. Y., Jr., 491(74,75), 496(75), 530 (75), 549(74), 550(74), 572(74,75), 573 (74,75), 600
- Bassin, M., 491(102), 501(102), 524(102), 525(102), 600
- Basu, R., 45(137), 75, 96(96), 128, 168(15), 209
- Batt, L., 256(235), 265(235), 294
- Battegay, M., 179(50), 210
- Batterham, T. J., 383(217), 479
- Batty, L. B., 304(23), 341(190), 343, 348
- Bauder, A., 38(125), 74
- Baudet, P., 516(336,337), 520(336,337), 606
- Baudisch, O., 222, 288
- Bauer, E., 272(355), 273(355), 297
- Bauer, K., 417(389), 422(389), 483, 597 (586), 612
- Bauer, L., 257(240), 294
- Baumgartner, P., 220(23), 288
- Baur, E., 661, 683
- Bax, C. M., 65(202), 76
- Bayer, R. P., 151(47), 162, 253(224), 294
- Bayliss, N. S., 34(109), 45, 74, 75, 167(7), 209
- Bazhenova, L. M., 102(118), 129
- Beach, J. Y., 32(103), 74
- Beaton, J. M., 221(34), 288
- Bebbington, A., 517(347), 606
- Becker, D., 181(58), 210
- Becker, G., 491(40), 501(40), 523(40), 529 (40), 599
- Beckwith, A. L., 491(121,130), 494(121), 510(121), 511(121), 540(121,130), 544 (121), 546(121), 566(130), 569, 601
- Bedard, M., 673–675(139), 684
- Becars, W. L., 333(159), 347
- Beevers, C. A., 674(159), 684
- Beger, J., 232(90), 286(435), 290, 299
- Behr, L. C., 469(481), 486
- Behrend, R., 256(236), 294
- Beier, T., 231(87), 290
- Bekker, R. A., 231(83), 290
- Bekkum, H. van, 59, 76, 534(404), 551 (404), 608
- Belew, J. S., 243(157), 292, 366(114), 373 (114), 374(114), 468(478a), 476, 486
- Belikov, V. M., 306(32), 343, 353(38–43), 354(39,55), 356(39,42,55), 364(40,42), 365(40), 366(38,39,42,55), 367(139), 372



- Belikov, V. M. (*continued*)  
 (55), 373(38-40, 55), 374(150,151), 376  
 (158), 383(150), 472(38), 474, 476, 477
- Bell, R. P., 364, 365(111), 367(111), 368  
 (111,124,125), 375(154,155), 411(362),  
 476, 477, 482
- Bellamy, L. J., 69, 77, 80(1), 82(1), 83, 86,  
 88(1), 89(1), 90(1), 125, 126, 138(2),  
 139(2), 161, 383(215), 479
- Bellobono, I. R., 102(130), 129
- Beltrame, P., 491(186-189), 492(186,187),  
 494(186,188,189), 578(186), 579(186-  
 189), 580, 581(189), 602
- Belyaevskaya, N. M., 86(36), 126
- Belzecki, C., 229(76), 289
- Bender, M. L., 350(5), 417(5,388,393,397),  
 422(393,397), 426(5,388,393,397), 427  
 (5,388,393), 445(393), 449(5,388,393),  
 473, 483
- Benedikt, R., 226(62), 289
- Benewolenskaja, S. W., 354(79), 475
- Ben Hur, D., 354(72), 475
- Benkovic, P. A., 573(506), 610
- Benkovic, S. J., 573(506), 610
- Benn, M. H., 332(158), 347
- Benson, F. R., 470(486), 486
- Beranek, E., 558(430), 608
- Berckmann, V. S. F., 542(394), 608, 565  
 (468), 608, 609
- Berg, A., 617, 681
- Bergman, P. M., 151(47), 162, 253(224),  
 293
- Bergmann, E., 276(373), 297
- Berk, P. van, 493(281), 505(281), 539(281),  
 541(281), 605
- Berliner, E., 505(308), 533-535(308), 542  
 (395), 578-580(395), 605, 608
- Bernal, I., 58(182), 76, 124, 135
- Bernard, R. E., 270(336), 296
- Bernasconi, C., 377(174), 477, 491, 498  
 (36), 501(32-37,39,40), 503(78), 504(33,  
 34,36), 507(78), 521(78), 522(34,35), 523  
 (34,35,37,40), 524(36), 525(34,36,38,78),  
 526(78), 528, 529(34-40), 530(34,35,78),  
 571(78), 576(78), 599, 600
- Berndt, D. C., 391(270), 480
- Bernstein, H. J., 54(154), 75
- Berry, E. J., 417(397), 422(397), 426(397),  
 483
- Bersohn, M., 428(429), 445(429), 484
- Berson, J., 181(60), 186, 210, 246(177), 292
- Bertels, K., 264(298), 295
- Berther, C., 241(142), 291
- Berthier, G., 18(46), 20(48), 21, 22, 68(48),  
 69, 72, 73
- Bertini, V., 102(133), 130
- Berzina, I. N., 102(125), 129
- Bethoux, M., 21(61), 73
- Bettinetti, G. F., 271(346), 297
- Bevan, C. W. L., 491, 492(26), 493(22),  
 494(18), 495(18,20,22), 496(18,20,22),  
 497(30), 500(23), 501(30), 504(30), 505  
 (23), 508(18,20,22-24), 509(20,22,25,28),  
 510(18,24), 511(18,21,23), 512(27), 513  
 (27), 514(23,27), 516(29), 517(29), 529  
 (30), 531(27), 534(20,28), 535(20,28), 537  
 (20), 538(25), 539(21), 541(25,29), 544  
 (19), 545(29,30), 546(24,30), 547(23), 549  
 (29), 550(29), 552(30), 578(30), 598, 599
- Beynon, J., 181(56), 182(69), 210
- Bezhashvili, K. A., 115(251), 133
- Bhaskar, K. R., 100(100), 120, 129, 134,  
 137
- Bickborn, B., 557(422), 608
- Bickel, H., 138(139), 346
- Bie, D. A. de, 491(270), 605
- Bielski, B. H. J., 122(305), 134, 172 (26),  
 209
- Bier, A., 557(420), 558(420), 608
- Binnie, W. P., 670(130), 684
- Birchall, J. M., 218(8), 265(311), 266(320),  
 287, 296
- Bird, G. R., 23(71), 32, 73, 74
- Biryukova, L. I., 373(145), 374(145,156),  
 375(156), 477
- Bishop, R. R., 491(81), 497(81), 504(81),  
 518(81), 520(81), 550(81), 551(81), 581  
 (81), 600
- Blacet, F., 172(32), 209
- Black, A. P., 310(48), 344
- Blackburn, D. E., 213
- Blackley, W., 206(130), 212, 255(233), 294
- Blackwood, R. K., 325(126), 326(126), 329  
 (149,150), 330(149-152, 155), 331(151),  
 332(149-152), 333(151), 334(150), 346,

- 347, 366(116), 373(116), 374(116), 376  
(116), 429(434), 476, 484
- Blagoveshchenskii, V. S., 248(191), 292
- Blanchard, K. C., 625(53), 626(54), 682
- Blandamer, M. J., 124(317), 135
- Blangey, L., 226(57), 289
- Blatt, A. H., 250 (197), 293
- Blecker, L. R., 380(192), 411(192), 412  
(192), 478
- Blickenstaff, R. T., 302(12), 340(12), 343
- Bloch, S., 321(104), 345
- Bloom, A. J., 218(8), 265(311), 266(320),  
287, 296
- Bluhm, A., 175(41), 176(41), 191, 199,  
204(123), 209, 211, 212, 354(74,75,80),  
355(75,82), 383(74,75), 475
- Blumberg, S., 90(74), 128
- Boberg, F., 434(442), 485
- Bobovich, Y. S., 84(27), 86(36), 91(82),  
116(262), 125(344), 126, 128, 133, 135,  
362(89), 475
- Boer, T. de, 203, 204(121), 205(121), 211,  
212, 487, 595(570-575), 596(584), 612
- Bogdanov, S. V., 262(282), 295
- Boggs, J. E., 161, 163
- Boggus, J., 120(282), 134
- Boll, P. M., 144(24), 162
- Bolto, B. A., 491(122,132,133,139,140,145),  
492(139,140), 495(132), 508(132,139,140),  
509(132,139,140,145), 510(145), 511(132,  
145), 514(133), 515(145), 534(145), 536  
(139), 540(122,132,133,139,140,145), 541  
(132), 544(132), 546(132), 548(145), 564  
(122,139), 601
- Bolton, J. R., 124(320), 135
- Bolton, R., 491(149,151), 511(151), 515  
(151), 540(149,151), 601
- Bonciani, T., 263(294), 287(436), 295, 299
- Bonelli, R. A., 491(45), 502(45), 534(45),  
535(45), 599
- Bonetti, G. A., 378(179a), 478
- Bonnett, R., 453(455), 485
- Boos, W. F., 377(162), 477
- Booth, G. E., 363(102), 475
- Bordwell, F. G., 316, 317(84-87), 318(84),  
345, 363(92a), 365(92a), 367, 368-370  
(92a), 475
- Borek, F., 88, 127
- Borgardt, F. G., 335(171), 347, 460(460),  
485
- Born, M., 3, 71
- Bornhardt, C., 217(2), 287
- Borrows, E. T., 233(97), 290, 570(501), 610
- Borsche, W., 240(135), 291, 569(488,489),  
570(502), 572(502), 610
- Bosch, E., 260(256), 294
- Boschan, R., 313(60), 344
- Bose, M., 58(170), 75
- Boulton, A. J., 377(175), 478
- Bourdais, J., 495(288), 515(288), 516(288),  
554(288), 605
- Bourillot, M., 362(87), 475
- Bourns, A. N., 526(383), 529(383), 530  
(383,385), 531(383,385), 571(383), 607
- Bowering, W. D. S., 453(453), 485
- Bowers, A., 324(120,121), 333(120,167),  
346, 347, 363(93,94), 475
- Bowers, K. W., 123, 134
- Boyd, T., 302(6), 342
- Boyer, J. H., 215, 236(116), 239(116), 241  
(116), 247(116), 255(116), 261(271), 262  
(116,280,281), 264(303), 272(303), 275  
(281), 291, 295, 296
- Boyland, E., 242(150), 291
- Brachmann, K., 411(346), 482
- Bradley, W., 555(412), 608
- Brady, O. T., 494(283), 503(283), 504(283),  
550(283), 605
- Brain, D. K., 341(189), 348
- Branch, G. E. K., 353(34), 354(34), 356  
(34), 366(34), 373(34), 474
- Brand, J. C. D., 159(73), 163
- Brandmueller, J., 125(343), 135
- Brandt, P., 179(50), 210
- Bransford, J. W., 23(71), 32(71), 73
- Brassert, W., 225(53), 289
- Brasted, R. C., 391(271), 480
- Braude, E. A., 94(91), 128, 167(10), 209
- Brault, R. G., 354(78), 355(78), 475
- Braunitzer, G., 499(291), 605
- Braxton, H. G., 341(192), 348
- Brenner, J. E., 304(23), 343
- Breslow, R., 331, 332(156), 347
- Bret, G., 125(341), 135
- Bricker, C. E., 369(129), 370(129), 476

- Briegleb, G., 116, 117, 118(267), 119(267),  
120, 133, 134, 520(357), 558(433,434),  
571(433), 607, 608
- Brière, R., 15–17(42), 18(42,49), 19(42),  
20(49), 21(42), 70(42), 72, 73
- Brieux, J. A., 491, 494(41), 495(46), 496  
(41,43,44,47), 497(50), 498, 502(41,43–47,  
49–51), 503(43,44,46), 505(41), 506(41),  
514(49), 524(47,50,51), 529(51), 530  
(47,50,51), 531, 534(45,49), 535(45,49),  
537, 538(43,44), 540(49), 541(43,44),  
544(41), 550(49), 552(47), 553(46,50),  
599
- Briggs, A. A., 93(89), 104(89), 128
- Briggs, L. H., 111(216), 132
- Briner, G. P., 491(128,129), 495(128),  
507(129), 508(128), 509(128), 510(128,  
129), 511(128,129), 520(128), 540(128,  
129), 544(128), 554(129), 601
- Brion, H., 8(14), 9(14), 68(14), 72
- Brockman, F. J., 633(72), 682
- Brockway, L. O., 32(103), 74
- Brodskii, A. I., 125(330), 135
- Brois, S. J., 260(255), 294
- Bromberger, B., 266(317), 296
- Brook, A. J., 520(361), 558(361), 577  
(361), 607
- Brooks, S. G., 303(18), 343
- Broser, W., 125(331), 135
- Brosowski, K. H., 268(328), 271(328), 278  
(328), 296
- Brower, K. R., 536(391,392), 607
- Brown, E., 181(60), 186, 210, 246(177),  
292
- Brown, E. V., 582(537), 611
- Brown, G. B., 405(327), 406(327), 423  
(417), 429(327,417), 445(417), 450(417),  
482, 484
- Brown, H. A., 222(36), 288
- Brown, H. C., 372(152), 376(152), 477
- Brown, H. W., 156, 163
- Brown, J. F., 82(8), 83, 84(8), 85, 88–90  
(8), 126, 182(70), 210, 218(15), 265(308),  
287, 296
- Brown, M. S., 354(77), 355(77), 475
- Brown, R. A., 352(23), 385(222), 386(222),  
389(222), 390(222), 417(23,391), 418–420  
(23), 422–424(23), 435–437(23), 438(222),  
440(222), 441(222), 447(23), 451(23),  
459(23), 473, 479, 483
- Brown, R. D., 24(78–80), 71(226), 73, 77
- Brown, T. H., 59, 76
- Brown, W. G., 101(102a), 129
- Brownlie, I. A., 139, 161
- Brownstein, S., 622(33), 681
- Bruck, W., 570(449), 610
- Bruckner, A., 229(75), 289
- Bruckner, V., 322, 345
- Brück, B., 380(191), 383(213), 414(191,  
213,382), 415(213), 418(191), 419(191),  
420(191,213), 421(213), 422(191), 423  
(191), 424(213), 436(213), 437(213),  
444(213), 447(191,213), 478, 479, 483
- Bruice, T. C., 364(111a), 476
- Brunel, Y., 21(56), 73, 304(23), 343
- Brunet, P. E., 673(152), 684
- Bruni, G., 275(369), 297
- Brunings, K. J., 101(103), 129
- Bruno, J. J., 491(111), 497(111), 503(111),  
524(111), 525(111), 600
- Bryden, J. H., 674(160), 684
- Buchanan, M. N., 627(55,56), 641(56), 682
- Buchi, G., 192, 211
- Buckingham, A. D., 111(211), 132
- Buckwald, K. W., 673(145), 684
- Buczowski, Z., 84(21), 88(51), 126, 127
- Budagvants, M. I., 410(343,344), 421(344),  
424(344), 448(344), 482
- Budzikiewicz, H., 181(57,58), 210
- Bühler, E., 582(531), 611
- Büsdorf, H., 260(257), 271(348), 272(348,  
352), 294, 297
- Bugai, P. M., 102(118), 129, 153(61), 163
- Bulka, E., 277(387), 298
- Bull, J. R., 111(219), 132, 302, 303(16),  
306(16), 307(16), 323(16), 330(16), 343
- Bunce, N. J., 213
- Buncel, E., 556(419), 558(419), 608
- Bungs, J., 408(336), 412(336), 413(336),  
482
- Bunnenberg, E., 37(119), 74, 155(65), 163,  
167(8), 209
- Bunnett, J. F., 377(168,174), 477, 490–492,  
493(1), 495(1,58,59,61), 496(58,60,75),  
497, 498(58), 500(73), 501(67,72,73,76),  
502(58,59), 503(55,58–60,67,68,78), 504

(60,68,71,72), 505(53), 505(67), 506  
 (67,68,72) 507(55,73,78), 508(70,73), 509  
 (53,70,73), 510(53-55,70,71), 511(54),  
 512(71), 514(55,61,70,73), 517(69), 518  
 (71), 520, 521(78), 522(76), 523(72,76),  
 524(72), 525(68,78), 526(68,78), 527(68),  
 528, 530(56,68,72,75-78), 531, 533, 534  
 (53,54,61), 540(1,59), 541(72), 542(67),  
 545(67,69,70,72), 547(55,70,71), 549, 550  
 (73,74), 552(10), 554(10,58,60,68), 556(1),  
 564(67,70), 565, 568(479), 571(67,68,70,  
 78), 572(67,74,75), 573(67,74,75), 575  
 (70), 576(67,68,70,78), 588, 589, 591(52),  
 592, 598-600, 610, 612

Bunton, C. A., 622(33), 681

Bunyan, P. J., 263(292), 295

Burawoy, A., 151, 152, 162

Burdon, J., 496(285), 497(285), 500(285),  
 508(285,318), 554(318), 605, 606

Burgess, H., 411(360), 482

Buriks, R., 262(280), 295

Burke, K. A., 326(133), 346

Burkhard, C. A., 265(308), 296

Burkhardt, G. N., 276(371), 297

Burkhardt, L. A., 674(160), 684

Burns, R. G., 503(304), 504(304), 507  
 (304), 508(304), 509(304), 510(322),  
 514(304,322), 554(304,322), 605, 606

Burrows, B. F., 320(100), 345, 390(265),  
 480

Burrus, C. A., 8(13), 72

Burtner, R. R., 308(38), 343

Busch, M., 225(55), 260(251), 289, 294

Bussell, G. E., 491(56), 530(56), 599

Buu-Hoi, N. P., 90(61), 127

Bye, G. C., 491(19,22,24), 493(22), 495(22),  
 496(22), 508(22,24), 509(22), 510(24),  
 544(19), 546(24), 598

Bykhovskaya, E. G., 271(344), 297

## C

Cadogan, J. I. G., 263(292), 295

Cady, H. H., 674(161), 684

Cahn, R. S., 569(497), 610

Cain, J. C., 242(147), 291

Cain, R. B., 251(210), 293

Cais, M., 151(48), 152(55), 162, 163

Caldin, E. F., 377(171), 477, 520(352-354,  
 361), 521, 558(353,361,429), 575(429),  
 577(361,429), 606-608

Caldwell, K. S., 423(415), 428(415), 460  
 (415), 484

Callahan, J. J., 582(528), 611

Calvello, E., 233(95), 280(406), 290, 298

Calvert, J., 166, 167(2), 170(2), 174(38),  
 186(38), 208(141), 208, 209, 212, 218(4),  
 220(27), 287, 288, 584(543), 611

Calvin, M., 195, 198, 211, 465(477), 470  
 (477), 486

Cambie, R. C., 111(216), 132

Cameron, J., 207, 208(138), 212

Cammarata, A., 254(230), 294

Campbell, N., 579(521), 611

Campbell, R., 102(126), 111(226), 129,  
 132, 176(43), 209, 411(348), 482

Campbell-Crawford, A. N., 383(219), 415  
 (219), 479

Canback, T., 560(439), 609

Candel-Vila, R., 671(133), 684

Caneda, R. V., 491(50,51), 497(50), 502  
 (50,51), 524(50,51), 529(51), 530(50,51),  
 531(50,51), 553(50), 599

Canonica, L., 378(183), 478

Canter, M., 558(434), 608

Capindale, J. B., 115(255), 133

Caple, R., 363(96), 475

Capon, B., 490, 491(86,89), 502(89), 504  
 (86), 505(86), 509(89), 510(86,89), 511  
 (86), 529(11,13), 533(86), 538(89), 540  
 (89), 541(89), 598, 600

Cardwell, H. M. E., 376(157), 477

Carmack, M., 664(125), 673(150), 683, 684

Carmody, D. J., 265(312), 296

Caro, H., 223(42), 288

Caron, A., 23(66,67), 73

Carpenter, G. B., 23(70), 73

Carpignano, R., 102(117), 129

Carrà, S., 491(190,191,193), 493(190), 503-  
 506(190), 510(190), 511(190), 520(190),  
 532(190,191,193), 579(190), 602

Carrington, A., 17(45), 59(45), 72, 124  
 (319), 135, 182(65), 210

Carstens, E., 250(198), 293

Carter, R. E., 55(158), 75

Cartwright, N. J., 251(210), 293

- Casario, M. C., 331(157), 347  
 Castelli, A. H., 84, 126  
 Castorina, T. C., 662  
 Castro, A. J., 49(149), 498(49), 502(49), 514(49), 534(49), 535(49), 537(49), 540(49), 550(49), 599  
 Castro, C. E., 120(278), 134  
 Cavell, E. A. S., 491(81,82), 497(81), 504(81,82), 518(81,82), 520(81,82), 550(81,82), 551(81), 581(81,82), 600  
 Caveng, P., 491(379-381), 531(379-381), 607  
 Cazeneuve, P., 411(351,352), 482  
 Cerda, E., 238(125), 291  
 Cerniani, A., 569(494), 571(494), 576(494), 610  
 Cesaroni, M. R., 278(392), 279(392), 298  
 Chaberek, S., 274(367), 297  
 Chachaty, C., 213  
 Chain, E. B., 251(211), 293  
 Chakraborty, A. K., 125(345), 135  
 Chalmers, M., 325(127), 327(127), 328(127), 346  
 Chamberlain, J. T., 151(48), 152(55), 162, 163  
 Chambers, J. Q., 124(314), 135  
 Chan, S., 172(33), 173(33), 209  
 Chan, T. L., 491(155), 514(155), 534(155), 540(155), 601  
 Chandra, A. K., 102(114), 129  
 Chapman, F., 628(59), 633, 682  
 Chapman, N. B., 491, 495(85), 496(85), 497(79,81), 500(85), 501(79,80), 502(80,85,89), 504(79,81,82,86), 505(79,80,85,86), 506(79,85), 509(89), 510(86,89), 511(86), 518(79,81,82,87), 520(79,81,82,87), 529(79), 531(87), 533(86,87,90), 538(89), 540(89), 541(89,90), 542(85), 544(85), 545(79), 546(79), 550(81,82,90), 551(79,81,90), 552(79), 581(81,82), 582(84), 600  
 Chapman, O., 176, 177(44,46), 178(46), 179(48), 180(48), 181, 199, 208, 209, 210, 221(32), 288, 251(205), 293, 388(234,235), 389(234,235), 479  
 Charton, J. L., 212, 213  
 Chattaway, F. D., 435(447), 485  
 Chatterjee, N., 58(170), 75  
 Chaudbury, D. K., 491(90), 533(90), 541(90), 550(90), 551(90), 600  
 Chauvin, M., 151(52), 162  
 Chavan, J. J., 310(50), 344, 406(329), 407(329), 411(329), 412(329), 482  
 Chédin, J., 631(68), 637(68), 682  
 Chehada, M., 90(58), 127  
 Chelobov, Z. N., 274(364), 297  
 Chelsea, R., 250(201), 293  
 Chem, M. C., 88(50), 111(50), 127  
 Chen, M. M., 121(298), 134  
 Cherkasov, A., 180(54), 210  
 Cheshko, R. S., 491(264), 505(264), 604  
 Chesnut, D. B., 20, 59(47), 72  
 Chick, M. J., 360(86a), 475  
 Chilton, H. T. J., 218(5), 252(214), 255(214), 256(5), 287, 293  
 Chlenov, I. E., 84(22), 126, 418(398,400), 435(449), 453(398,400, 456-458), 454(398,456), 455(398,400,456), 456(398, 456,458), 457(456-458), 458(398,400, 456, 457,458a), 459(400,457), 483, 485  
 Chojnacki, C., 325(123), 335(123), 346  
 Chow, Y. L., 230(81), 290  
 Christ, H. A., 58(172), 76  
 Christie, M. I., 218(6,7), 219(18), 265(310), 287, 288, 296  
 Christman, F., 266(316), 296  
 Chuang, L., 263(290), 295  
 Chur, M., 283(417), 298  
 Chute, W. J., 629(66,67), 633(66), 650(110), 655(113), 660(113), 682, 683  
 Chvapl, M., 145(29), 162  
 Ciamician, G., 183, 186(75), 210, 246(176), 278(388), 292, 298  
 Clague, A. D. H., 104(158), 130  
 Clapp, L. B., 468(478a), 486  
 Clark, D. T., 110(210), 111(210), 132  
 Clark, V. M., 453(453,455), 485  
 Clayton, A., 673(141), 684  
 Clayton, J. C., 570(501), 610  
 Clemens, L. M., 520(358,359), 607  
 Clementi, E., 25, 73  
 Cleveland, P., 177(46), 178(46), 210  
 Clifford, D. P., 377(175), 478  
 Cloëz, C., 223(45), 288  
 Closs, G. L., 260(255), 294  
 Clunie, J. C., 368(124), 476

- Clutter, R. J., 242(148), 291, 309(42), 310(42), 343  
 Coats, R. R., 588(550), 611  
 Coburn, M. D., 102(134), 130  
 Coburn, W. C., Jr., 70(222), 77  
 Cochran, J. C., 510(321), 524(321), 606  
 Coe, C. S., 399(301), 481  
 Coffman, D. D., 319(97), 345  
 Cohen, H. L., 670(130), 684  
 Cohen, L. A., 116(264), 133, 424(420a), 484  
 Cohen, M. S., 234(104), 290  
 Cohen, V. W., 121(296), 134  
 Cohn, G., 258(242), 294  
 Coleman, G. H., 223(43), 240(128), 288, 291  
 Collier, R. E., 591(558), 612  
 Collin, J., 31(98), 74, 206(132), 212  
 Collins, J. M., 219(18), 288  
 Colonna, M., 277(381), 298  
 Colter, A. K., 520(358,359), 607  
 Colthup, N. B., 80(3), 82(3), 126  
 Colwell, C. E., 335(175), 338(179), 347, 404(323), 481  
 Combe, W. P., 581(526), 611  
 Conduit, C. P., 85(34), 86, 101(34), 126  
 Connerade, E., 416(386), 422(386), 423(386), 483  
 Connor, T., 634(77), 682  
 Conrad, F., 319, 345, 418(408), 422(408), 432(408), 436(408), 484  
 Considine, W. J., 238(124), 291  
 Convert, O., 388(179), 478  
 Cook, D. J., 386(233), 388(233), 479  
 Cooke, P. W., 119(277), 134  
 Cooke, R. G., 356(61), 360(61), 474  
 Cooley, J. H., 386(240), 388(240), 389(240), 479  
 Coombes, G. E. A., 212  
 Coppens, P., 124(323), 135  
 Coppers, P., 246(181), 292  
 Cordes, H. F., 353(52), 356(52), 357(52), 360-362(52), 366(52), 371-373(52), 383(52), 473(52), 474  
 Cormack, J. F., 491(52), 549(52), 591(52), 592(52), 599  
 Cornelisse, J., 491(275), 605  
 Cornelius, J., 200(106), 211  
 Cortier, J., 512(327), 513(327), 531(327), 544(327), 545(327), 606  
 Costain, W., 674, 684  
 Cott, W. J., 327(135), 346  
 Cottrill, E. L., 234(104), 290  
 Coulson, C. A., 24(81), 25(81), 73  
 Cowan, J. C., 232(92), 290  
 Cowell, G. W., 213  
 Cowley, D. J., 213  
 Cox, E. G., 674, 684  
 Coyne, D. M., 219(61), 288  
 Cram, D. J., 577(422), 608  
 Crampton, M. R., 111(224), 120(283), 132, 134, 377(167), 477, 491(204-210), 521(204-210), 557(206), 558(204, 206-208), 566(206,209), 567(204,206,209), 575(205, 206,209), 580(205), 587(204), 602, 603  
 Crandall, E. W., 104, 130  
 Crater, W. de C., 649(109), 670(109), 683  
 Craven, J. M., 101(109), 129  
 Crawford, G. H., 218(13), 222(39), 287, 288  
 Creegan, F. J., 259(244), 294  
 Cresswell, W. T., 675(168), 676(168), 684  
 Criner, G. X., 235(112), 238(123), 290, 291, 304, 305(26), 306(25), 343  
 Crockford, H. D., 491(66), 599  
 Cromer, D. T., 674(161), 684  
 Cronmeyer, D. C., 125(346), 135  
 Cronheim, G., 223(41), 288  
 Crooker, J. F., 627(55), 682  
 Cropper, F. R., 494(283), 503(283), 504(283), 550(283), 605  
 Cruickshank, D. W. J., 23(72), 73  
 Crumpler, C., 207(137), 212  
 Cullen, E., 594, 612  
 Culvenor, C. C., 576(517), 610  
 Cundall, R. B., 371(140a), 390(140a), 391(140a), 476  
 Curl, R. F., Jr., 23(71), 32(71), 73  
 Curry, H. M., 673(151), 684  
 Cusmano, G., 233(99), 260(247), 290, 294  
 Cuta, F., 558(430,431), 608  
 Cuthrell, R. E., 104(161), 130  
 Czekalla, J., 42(135), 47, 75, 117, 120(282), 133, 134

## D

- Dabrowska, U., 114, 115, 133  
 Dacons, J. C., 340(185), 348  
 Dadien, A., 670(131), 684  
 Dahne, A., 87(38), 126  
 Dailey, B. D., 106, 131  
 Dailey, B. P., 54(155), 55, 56, 57(163), 75, 108(196), 109(197,198), 131  
 Dains, F. B., 261(263), 294  
 Dale, B., 119(274), 133  
 Dale, C., 402(310), 405(310), 481  
 Daly, L. H., 80(3), 82(3), 91(79), 126, 128  
 Daly, N. J., 491(147), 492(147), 509(147), 510(147), 536(147), 540(147), 601  
 D'Amico, J. J., 223(44,46), 288  
 Danen, W., 190(85), 192, 210, 402(314), 406(314), 422(314), 426(314, 428a), 428(314,428a), 481, 484  
 Daniele, G., 220(24), 288  
 Daniels, R., 325(127), 327(127), 328(127), 346  
 Danilova, V. I., 102(116), 113(232), 115(254), 129, 132, 133  
 Danzig, M. H., 302(10), 343  
 Danzig, M. J., 240(137), 262(281), 275(281), 291, 295  
 Darling, S. F., 341(194), 348, 429(438), 430(438), 433(438), 485  
 Darwin, C., 252(216), 293  
 Das, N., 58(170), 75  
 Da Settimo, A., 111(225), 132  
 Daudel, R., 7(10), 71(225,227), 72, 77  
 Daulton, H. L., 319(91), 345  
 Davidson, J. S., 237(119), 291  
 Davies, M., 671(134), 684  
 Davies, W., 576(517), 610  
 Davis, B. A., 283(419), 298  
 Davis, G. T., 491(55,71), 503(55), 504(71), 507(55), 510(55,71), 512(71), 514(55), 518(71), 547(55,71), 588(55), 599  
 Davis, H. R., 151(47), 162, 244(165), 253(224), 265(165), 292, 293  
 Davis, T. L., 625-627, 682  
 Deaniker, H. U., 225(56), 289  
 Dearden, J. G., 114(238), 132  
 Dearman, H. H., 59(189), 76  
 DeButts, E. H., 260(250), 294  
 Decker, H., 272(355), 273(355), 297  
 Degering, E. F., 386(229), 388(229), 438(229), 439(229), 447(229), 460(229), 479  
 Degner, O., 620(28), 638(28), 640(28), 681  
 Degtyarev, L. S., 125(330), 135  
 Deguchi, Y., 68(213), 76, 121(297), 134  
 Degurko, T. A., 576(516), 610  
 Dehn, J. S., 335(174), 336(174), 347  
 De Jongh, R., 200(102,104,105), 211, 212  
 Dekker, A. O., 673(154), 684  
 Del Cima, F., 491(94,95), 500(95), 501(94), 504(94), 525(94), 533(94), 541(94,95), 542(94,95), 545(94), 600  
 Del Pesco, T., 202(114), 211  
 Delpierre, G. R., 352(24), 453(24), 470(24), 473  
 De Malde, M., 220(24), 288  
 Deno, N. C., 667(127), 683  
 Desai, S. C., 614(15), 616(15), 628(15), 681  
 DeSavigny, C. B., 378(179a), 478  
 Desch, C. H., 411(358), 482  
 Desch, G. H., 673(140), 684  
 Descotes, G., 362(87), 475  
 Deshapande, S. S., 232(91), 290  
 Dessauer, R., 191(87), 211  
 Destro, R., 491(192), 567(192), 602  
 Deswarte, S., 353(46,49), 385(46), 386(46), 474  
 Deulofeu, V., 491(41-44), 494(41), 496(41, 43,44), 502(41,43,44), 503(43,44), 505(41), 506(41), 538(43,44), 541(43,44), 544(41), 599  
 DeVries, T., 472(490), 486  
 Dewald, M., 235(113), 238(113), 290, 469(480), 486  
 Dewar, M. J. S., 118(270), 133  
 Deyrup, A. J., 284(426), 299  
 Dickey, J. B., 620(30), 621(30), 638(30), 681  
 Dickinson, W. B., 248(187), 292  
 Didonna, S., 233(99), 290  
 Dieffenbach, O., 244(159), 292  
 Diehl, P., 55, 58, 75, 76  
 Diepolder, E., 224(52), 289  
 Dietrich, H., 15(31), 72, 252(216), 293  
 Dietschy, R., 245(174), 292  
 Dietz, G., 250(198), 293  
 Digioia, N., 263(294), 295

- Dillon, R. L., 356(56,57), 364(57), 365(57),  
366(56), 367(57), 372(57), 373(56), 374  
(56), 376(56), 474
- Dilthey, W., 271(343), 297
- Dimroth, K., 195(96), 211
- Dinulescu, I. G., 402(309), 481
- Dinwoodie, A., 206(131), 212, 255(232),  
294
- Dionis'ev, V. D., 105(169), 131
- Dirac, P. A. M., 2(1), 71
- Dirkx, I. P., 487
- Dissel, S. van, 622(34), 639(34), 681
- Dittmer, D. C., 261(262), 294, 552(400),  
608
- Dixon, R. N., 148(41), 162
- Dixon, W. B., 106(182), 131
- Djerassi, C., 21(57), 37(119), 73, 74, 155,  
163, 167, 181(57,58), 209, 210
- Dobosz, T., 390(268), 391(268), 480
- Doering, W. E., 228(71), 289, 596(576,  
577), 612
- Dolk, L. A., 88(50), 111(50), 127
- Doll, W., 321(107), 345
- Dollfuss, F. E., 614(7), 619(7), 642(7), 681
- Dombrowski, A., 314(64), 344, 412(368),  
413(368), 482
- Dominikiewicz, M., 665(126), 683
- Donaruma, L. G., 219(22), 265(312), 288,  
296, 391(272,273), 417(390), 422(390),  
446(390), 480, 483
- Donath, J., 390(258), 391(258), 480
- Donnan, F. G., 326(133), 346
- Donohue, J., 23(66,67), 73, 674(160), 684
- Donovan, C. K., 259(244), 294
- Dorant, K., 198(100), 211
- Dorion, G. H., 379(185), 478
- Dormidontova, N. V., 230(78), 289
- Dornow, A., 433(439,440), 434(442), 460  
(465), 485
- Dorsky, J., 302(9), 343
- Dorst, W., 200(102), 211, 491(266), 582  
(266), 583(266), 604
- Doub, L., 50, 75
- Doumani, T. F., 399(301), 481
- Douthit, R. C., 90(69), 128
- Downing, D. C., 633(72), 650(110),  
682, 683
- Downing, D. T., 510(320), 606
- Dox, A. W., 315(76), 344
- Drake, N. L., 325-327(124), 346
- Draper, F., Jr., 491(53), 505(53), 509(53),  
510(53), 534(53), 599
- Dremin, A. N., 125(338), 135
- Dresdner, R. D., 243(158), 292
- Drozd, V. N., 589(552), 611
- Drumm, P. J., 568(482), 610
- Dubansky, A., 240(133), 270(133), 291
- Dubinskaya, E. I., 102(112), 129
- Dubois, J., 168(19), 209
- Dubov, S. S., 267(322), 296
- Dubsky, J. V., 628(60), 629(61), 682
- Duchesne, J., 24(81), 25(81), 73
- Duden, P., 428(432), 484, 661(119), 683
- Dufraisse, C., 90(77), 127, 179(49), 210
- Dull, M. F., 462(470), 463(470), 466  
(470), 485
- Dummel, R. J., 582(535), 611
- Dunderdale, J., 82(7), 126, 140(16), 162
- Dunn, G. E., 629(65,66), 633(66), 682
- Dunning, K. W., 657(117), 658(117), 683
- Dunning, W. J., 657(117), 658(117), 683
- Dupeyrat, R., 125(340), 135
- Dupeyre, R. M., 17(44), 18(49), 19(44), 20  
(49,50), 21(44,50), 72, 73
- Dupont, G., 318(88), 345
- Durocher, G., 115(253), 133
- Duynstee, E. F. J., 228(68), 289
- Dyall, L. K., 115, 133, 520(366), 567(366),  
607
- Dyatkin, B. L., 231(83), 237(118), 240  
(136), 270(340), 271(344), 284(118), 285  
(118), 290, 291, 296, 297, 378(184a), 478
- Dykhno, N. M., 558(428), 608

E

- Eakman, J. M., 363(106), 476
- Earl, J. C., 144(25), 145(25), 153(58), 162,  
163
- Earle, R. B., 377(164), 477
- Ebata, M., 261(276), 295
- Ebenroth, A., 232(90), 286(435), 290, 299
- Ebisu, K., 304(23,24), 341(190), 343, 348
- Eble, M., 650, 660
- Eckstein, Z., 84(24), 90(67), 126, 127



Edgerton, P. J., 542(395), 578-580(395), 608  
 Edwards, J. O., 264(302), 295, 552(401-403), 608  
 Edwards, W. G. H., 424(419), 444(419), 484  
 Egami, F., 261(276), 295  
 Egerts, V., 103(143), 130  
 Eglinton, G., 237(119), 291  
 Egorov, Yu. P., 353(43), 395(286), 396(286), 474, 480  
 Eholzer, U., 277(386), 298  
 Ehrlich P., 258(242), 277, 294, 298  
 Eidus, V. A., 102(124), 129  
 Eiduss, J., 102(131), 130, 412(370,371), 413(370,371), 483  
 Eidys, J., 88(47), 127  
 Eisenlohr, F., 675(167), 678(167), 684  
 Elder, E., 120(282), 134  
 Eldridge, S. J., 428(431), 484  
 Elger, F., 186(79), 188, 210  
 Elias, D. H., 492(282), 578, 579(282), 580(282), 581, 605  
 Eliel, E. L., 509(319), 510(319), 606  
 Ellers, J. C., 333(168), 347  
 Ellzey, S. E., Jr., 261(271), 264(303), 272(303), 295, 296  
 Elvert, H., 310(46), 344, 380(196), 403(196), 404(196), 417(196), 420(196), 422(196), 478  
 Elving, P. J., 263(290), 295, 368(122), 370(122), 476  
 Emerson, W. S., 262(278), 295  
 Emery, T., 240(132), 260(248), 291, 294  
 Emmons, W. D., 111(227), 132, 306, 307(30,34), 308, 309(43), 315(77-79), 320(99,101), 326(132), 333(163), 343-347, 378(184), 395(184), 418(401), 422(401), 423(418), 428(401,418), 429(418), 435(401), 438(401), 464(476), 478, 483, 484, 486, 615(17), 616, 628(17), 633(73), 681, 682  
 Emslie, P. H., 491(226-228), 516(226), 521(226-228), 566-568(226), 571(226), 575(226), 580(226), 603  
 Endres, A., 310(46), 344, 380(197), 403(197), 404(317), 444(197), 478, 481  
 Engel, P., 202(114), 211

England, B. D., 495(286), 503(304), 504(304), 507(304), 508(286,304), 509(286,304), 510(286,322), 514(304,322), 549(286), 554(304,322), 605, 606  
 Engler, C., 198(100), 211  
 Epishina, L. V., 374(151), 477  
 Erashko, V. I., 89(54), 127, 374(156), 375(156), 426(423c), 477, 484  
 Erickson, R. E., 243(156), 264(304), 292, 296  
 Erlandsson, G., 106, 131  
 Erlikh, R. D., 228(67), 260(67), 289  
 Ermolenko, I. N., 90(70), 128  
 Erp, H. van, 637(90,91), 638(91), 683  
 Errede, L. A., 151(47), 162, 218(11), 244(165), 253(224), 265(165), 287, 292, 293  
 Ershova, L. V., 374(150), 383(150), 477  
 Eskola, S., 321(107), 345  
 Espy, H. H., 284(421), 299  
 Esterowitz, L., 32(102), 74  
 Etheredge, S. J., 306(29), 343  
 Ettinger, L., 225(53), 289  
 Ettlinger, M. G., 332(158), 347  
 Euler, H., 618, 642, 681  
 Evans, D. H., 110(208), 132  
 Evans, R. M., 303(18), 343  
 Evans, W. J., 590(555), 611  
 Exelby, R., 191(86), 210  
 Eyring, H., 5(4), 6(4), 71

## F

Fabian, W., 331(156), 332(156), 347  
 Fabinyi, R., 259(243), 294  
 Fahim, H., 574(513), 610  
 Fainzil'berg, A. A., 89(54), 94(90), 127, 128, 340(184), 348, 366(115,117), 371(153), 373(115,117,145,146,148), 374(115,117,145,146,148,150,156), 375(153,156), 380(146), 383(150,206), 397(288,289), 418(402), 426(423c), 435(402), 460(464), 463(469), 467(469), 468(469), 476-478, 480, 481, 483-485  
 Faivush, M., 558(428), 608  
 Fanta, P. E., 414(379), 424(420), 447(420), 448(420), 483, 484, 582(534), 611  
 Farbenfabriken Bayer, 399(300), 481  
 Farberov, M. I., 230(78), 289

- Farmer, R. C., 377(173), 477, 511(324, 325), 567(325), 571(503), 575(503), 606, 610
- Farmer, V. C., 115(252), 133
- Farr, J., 356(60), 366(60), 373(60), 474
- Farrer, W. V., 283(418), 298
- Fassel, V. A., 85, 86(31), 89, 126
- Fava, A., 491(91), 500(91), 501(91), 504 (91), 522(91), 525(91), 530(91), 600
- Favini, G., 102, 129, 405(324), 481, 491 (182-185), 492(182), 507(184), 533(185), 579(182-185), 580, 602
- Fayita, T. O., 491(25), 509(25), 538(25), 541(25), 598
- Feather, J. A., 367(137), 476
- Fechtig, B., 328(139), 346
- Feigl, F., 273(358), 297
- Fein, M. M., 234(104), 290
- Feldman, A., 205(126), 211
- Feltkamp, H., 107, 108(191), 131, 363 (100,101), 475
- Fendler, J. H., 566(475), 567(475), 610
- Fénéant, S., 631(68), 637(68), 682
- Fenichel, L., 91(83), 128
- Fenimore, C. P., 148(40), 162, 252(216), 293
- Fenselau, A. H., 385(228), 479
- Feske, E., 240(135), 291, 570(502), 572 (502), 610
- Fetzer, U., 277(386), 298
- Feuer, B. I., 379(187), 478
- Feuer, H., 88-90(52), 107(188), 116, 127, 131, 311, 312(56), 316(81), 325(128), 327 (128), 328(128), 333(159,165), 335(175), 336(165), 338(165,179), 344, 346, 347, 353(50,51), 354(50,51), 356(50), 366 (50), 370(50,51), 371(51), 372(51), 373 (50), 380(192), 383(216), 385(50,51), 386 (51), 404(323), 406(330), 407(330), 408 (330,335), 409(330), 410(330), 411(192), 335,363), 412(192), 474, 478, 479, 481, 482
- Ficalbi, A., 354(70), 475
- Fick, R., 120(287), 134
- Fiedorek, F. T., 333(159), 347
- Fierens, P. J. C., 512(327), 513(327,331, 332), 520(351), 531(327,331,332,351), 539(332), 544(327), 545(327), 606
- Fieser, L. F., 314(64), 323, 344-346
- Fieser, M., 323(116), 345
- Filatov, A. S., 249(194), 263(194), 267 (194), 269(194), 293
- Filippo, P. A. S., 102(117), 129
- Filippova, A. K., 102(112), 129
- Finch, G. K., 144(22), 162
- Finckh, B., 673(146), 684
- Finger, G. C., 582(535a), 611
- Finger, R. C., 512(326), 513(326), 552 (326), 565(326), 606
- Finkel'shtein, A. V., 101(106), 129
- Finkelstein, M., 491(102,104,108,110), 496 (110), 497(110), 501(102), 502(110), 503 (104,108,110), 504(104), 524(102,104,108, 110), 525(102,104,108,110), 531(108,110), 553(110), 566(108), 600
- Finnegan, R. A., 213
- Finnegan, W. G., 485
- Firl, I., 270(338), 296
- Fischer, A., 504(305), 550(305), 551(305), 605
- Fischer, D., 508(318), 554(318), 606
- Fischer, E., 242(153), 292
- Fischer, H., 257(238), 294
- Fischer, H. O. L., 108(194), 131, 386(237, 238), 388(237,238), 479
- Fischer, M., 181(58), 210, 380(193), 403 (193), 404(193), 420(193), 422(193), 478
- Fischer, O., 224(52), 279(398,399,401), 282 (412,414), 283(417), 289, 298
- Fischer, P. B., 491(379), 531(379), 607
- Fischer, P. H. H., 63(195), 76, 124(324), 135
- Fishbein, L., 309(41), 325(130), 343, 346
- Flanagan, P. W. K., 105(167), 131, 234 (105), 290, 365(120), 367-370(120), 383(120,210), 476, 478
- Flett, M. S. C., 86, 126
- Fligge, M., 230(80), 232(89), 290, 322 (109), 345
- Flowers, W. T., 269(331), 296
- Fodor, G., 322(112), 345
- Förster, T., 50, 75
- Fohn, E. C., 104(161), 130
- Fokin, A. V., 248(191), 280(408), 286 (434), 292, 298, 299
- Foley, A. J., 491(26), 492(26), 598

- Folmer, O. F., 333(168), 347  
 Fong, F. K., 116(258), 133  
 Foote, C., 202(114), 211  
 Forbes, E. J., 116(260), 133  
 Forbes, W. F., 95-99(93), 100(93,101),  
 101(93), 114(238), 115, 128, 129, 132,  
 133  
 Forchioni, A., 213  
 Foreman, M. I., 491(226), 516(226), 521  
 (226), 566-568(226), 571(226), 575(226),  
 580(226), 603  
 Forsen, S., 116(259), 133  
 Forster, M. O., 304(21,22), 343, 381(201),  
 393(201), 394(201), 398(201), 478  
 Foss, M. E., 667(127), 683  
 Foster, R., 106(174,175), 111(215), 118  
 (271), 119(174,175,274,275), 120(284),  
 131-134, 219(17), 288, 377(165), 477,  
 490, 491, 501(216), 505(216), 506(216),  
 516(226), 520(220), 521, 531(17), 558  
 (212-216,218,221,222,224), 560(217,221,  
 223-225), 561(224,225), 564(216), 566  
 (221,226), 567(211,214,218,220-222,226),  
 568, 571(216,226), 573(216), 575(216,  
 226), 576(212,216), 577(216), 580(226),  
 598, 603  
 Fowler, J. S., 425(421a), 438(421a), 445  
 (421a), 451(421a), 484  
 Fox, D. L., 569(492), 610  
 Fox, W. M., 123(310), 134  
 Fraenkel, G. K., 55(158), 58(181-183),  
 59-61, 62(187), 75, 76, 124, 135  
 Francel, R. J., 85, 126  
 Franchimont, A. P. N., 614, 615, 621(31),  
 622, 623(41,42), 624(44), 628(60), 636  
 (79), 637, 638(92,93), 639(34,83,85,86,  
 94), 640(97), 642(101), 644(101), 671  
 (31), 673(143,144), 680-684  
 Francis, F., 664(124), 683  
 Franklin, N. C., 107, 108(191), 131, 363  
 (100,101), 475  
 Fraser, H. B., 362(88), 475  
 Fraser, R. R., 108(195), 131  
 Frazer, J. W., 266(318), 296  
 Frederick, M. R., 333(159), 347  
 Fredrick, J. L., 490, 581, 582(16), 598  
 Freed, J. H., 58(181), 76  
 Freeman, H. I., 333(162), 347  
 Freeman, J. P., 159, 160, 163, 238(122),  
 266(318), 291, 296, 303(19), 315(77-79),  
 320(101), 343-345, 383(211), 479, 615  
 (17), 616, 628(17), 681  
 Frei, J., 397(299), 398(299), 420(299), 424  
 (299), 447(299), 481  
 Freidlin, L. Kh., 244(164), 292  
 Freimanis, Ya., 412(373), 413(373), 483  
 Freman, W. A., 250(201), 293  
 Frenkel, Z., 272(355), 273(355), 297  
 Frennet, A., 513(332), 531(332), 539(332),  
 606  
 Frese, A., 433(440), 485  
 Freundler, P., 279(402), 298  
 Frey, S. W., 510(321), 524(321), 606  
 Freytag, H., 272(353), 297  
 Fried, I., 263(290), 295  
 Friedlander, P., 223(44), 288  
 Fries, D., 208(140), 212, 235(109,110),  
 236(110), 248(109,110), 290  
 Fries, K., 406(332), 411(332), 482  
 Frohberger, P. E., 240(127), 291  
 Frolov, Y. L., 102(112), 129  
 Frosin, V. N., 271(344), 297  
 Frost, H. V., 380(198), 460(198), 478  
 Frost, J. S., 218(6,7), 265(310), 287, 296  
 Fujii, H., 212  
 Fukui, K., 24, 25, 26(77), 29, 30, 31(77),  
 71(231,232), 73, 77, 332(164), 333(164),  
 347  
 Fukumoto, T., 281(410), 298  
 Fulde, P., 256(237), 294  
 Fuller, R. L., 391(270), 480  
 Fulmor, W., 111(221), 132, 312(57), 313  
 (57), 344, 406(334), 407(334), 409(334),  
 410(334), 482  
 Fumasoni, S., 230(79), 290  
 Funderburk, L., 367(136), 476  
 Furuya, Y., 229(73), 289  
 Fusco, R., 330(153), 332(153), 347, 646  
 Fyfe, C. A., 111(215), 120(284), 132, 134,  
 490, 491(17,221-224,227,228), 516(226),  
 521(221-224,227), 531(17), 558(221,222,  
 224), 560(221,223,224), 561(224), 566  
 (221,226), 567(221,222,226), 568(226),  
 571(226), 575(226), 580(226), 598, 603

## G

- Gabriel, S., 390(261), 391(261), 480  
 Gaines, W., 327(138), 346  
 Galli, R., 269(330), 296  
 Galvin, J. P., 219(21), 288  
 Gamba, A., 102(130), 129  
 Gambarjan, S., 261(267), 295  
 Gamper, J. R., 103(146), 130  
 Gapchenko, M. V., 261(268), 295  
 Garbisch, E. W., 316, 317(84-87), 318  
     (84), 345, 491(67), 501(67), 503(67),  
     505(67), 506(67), 520(67), 531(67), 542  
     (67), 545(67), 549(67), 564(67), 571-573  
     (67), 576(67), 599  
 Garbsch, P., 310(50), 344, 406(329), 407  
     (329), 411(329), 412(329), 482  
 Gardner, J. H., 230(78), 289, 319(95), 345  
 Garg, H. G., 505(310), 506(310), 564(310),  
     605  
 Garnovskii, A. D., 105(169), 131  
 Garnyuk, L. N., 125(330), 135  
 Garsaka, K. J., 90(69), 128  
 Garst, R. H., 491(76,77), 501(76,293),  
     522(76,293), 523(76,293), 526(293), 528  
     (76,77), 530(76,77,387), 571(293), 582  
     (387), 600, 605, 607  
 Garus, L. I., 491(239), 566(239), 568(239),  
     603  
 Gasnati, G., 391(274a), 392(274a), 469  
     (274a), 480  
 Gavars, R., 125(334), 135  
 Gazzolo, F. H., 377(163), 477  
 Geels, E., 191, 211, 262(284), 282(284),  
     295  
 Geger, V., 240(133), 270(133), 291  
 Geiger, E., 275(369), 297  
 Geiseler, G., 84, 126  
 Gelblum, E., 205(126), 211  
 Geller, B. A., 271(345), 282(415), 297, 298  
 Geller, L. E., 221(34), 288  
 Gelles, E., 375(155), 477  
 Genkina, E. V., 399(302), 481  
 George, J., 272(353), 297  
 George, M. V., 146(33), 160(33b), 162,  
     671(137), 674(137,162), 676(137,162),  
     684  
 Gerig, J. T., 530(387), 582(387), 607  
 Germain, G., 15(29,30), 72, 252(216), 293  
 German, L. S., 374(149), 477  
 Germane, S., 103(143), 130  
 Gerson, F., 63, 76  
 Geske, D. H., 58, 61-64, 76, 122(306),  
     123, 124(322a), 125(333), 134, 135  
 Geuther, A., 390(257), 480  
 Gevorkyan, A. A., 237(118), 270(340), 271  
     (344), 284(118), 285(118), 291, 296, 297  
 Ghersetti, S., 88(44), 127  
 Ghislandi, V., 155(66), 163  
 Giacobbe, G., 230(79), 290  
 Giarrusso, F. F., 37(120), 74, 305(28),  
     307(28), 343  
 Gibson, D. T., 588(550), 611  
 Gil, V. M. S., 57(168), 75  
 Gilbert, B. C., 68(214,215), 69(214,215),  
     76, 238(126), 291, 402(316), 481  
 Gillam, A. E., 102, 129  
 Giller, S. A., 102(124), 129  
 Gillers, S., 412(370,371), 413(370,371),  
     483  
 Gillibrand, M. I., 624(46), 682  
 Gillies, A., 661(123), 683  
 Gilman, H., 276(375), 297  
 Gilon, M., 512(327), 513(327), 531(327),  
     544(327), 545(327), 606  
 Ginsburg, V. A., 249(194), 263(194), 267  
     (194,322), 269(194), 285(429), 293, 296,  
     299  
 Gitel, P. O., 274(364), 297  
 Gitis, S. S., 377(172), 477, 491, 492(242),  
     511(234), 548(249), 558(247), 560(229),  
     235,236,245,250-252, 562(247), 564(247,  
     249), 565(230), 566(231-233,237,239,  
     242,244,248,253-255), 567(230,238,241),  
     568, 571(240,249), 576(249), 580(243),  
     603, 604  
 Glarum, S. H., 124(325), 135  
 Glaz, A. I., 491(230-232,238,239,241-244,  
     256), 492(242), 565(230), 566(231,232,  
     239,242,244), 567(230,238,241), 568, 580  
     (243), 603, 604  
 Glaz, A. Sh., 491(256), 604  
 Glazer, J., 224(49), 289  
 Gley, 646  
 Glier, R., 120(282), 134  
 Glover, D. J., 105(168), 131

- Glushenkov, V. A., 113(233), 132  
 Glusker, D. L., 141(18), 142(18), 162  
 Gluzinski, P., 84(24), 126  
 Goble, A. G., 34(113), 35(113), 74, 93(88), 128  
 Gohlke, R. E., 417(396), 422(396), 483  
 Gol'berkova, A. S., 102(118), 129  
 Gold, V., 120(283), 134, 201(111), 211, 367(137), 377(167), 476, 477, 491, 520 (197), 521, 557, 558(195,197,200,201, 204,206-208), 566(202,206,209), 567(196, 199,200,202,204,206,209), 575(197-199, 203,205,206,209), 580(205), 587, 602, 603  
 Goldish, E., 23(66), 73  
 Goldner, H., 250(198), 293  
 Goldschmidt, H., 260(254,258,259), 294  
 Goldschmidt, S., 266(316), 296  
 Goldstein, H., 470(487), 486  
 Golovaneva, A. F., 249(194), 263(194), 267(194), 269(194), 293  
 Golubenkova, A. M., 125(330), 135  
 Gombert, M., 260(253), 294  
 Gonikberg, M. G., 503(300-302), 533(300, 301), 536(302), 605  
 Goodall, D. M., 364(111), 365(111), 367 (111), 368(111), 476  
 Gordon, A. W., 309(40), 343  
 Gordon, J. E., 518(348,349), 554(348), 566(348), 571(348,349), 573(348), 606  
 Gorke, H., 415(384), 418-420(384), 422 (384), 423(384), 438(384), 483  
 Gorrington, A. M., 383(219), 415(219), 479  
 Gorwin, A. H., 101(103), 129  
 Goryacheva, N. S., 260(249), 283(249), 284 (249), 294  
 Goto, R., 203(120), 211  
 Gotshal, Y., 102(122), 129  
 Gotts, R. A., 405(325), 481  
 Gouch, T. E., 124(317), 135  
 Govindachari, T. R., 322(110,111), 345  
 Goward, G. W., 369(129), 370(129), 476  
 Gowenlock, B. G., 14(27), 72, 138(1), 139, 140(1), 141, 142(15), 143(15), 147(1), 149(44), 150(44), 161, 162, 211, 218(5), 252(214), 255(214), 256(5,235), 265(235), 284(422), 287, 293, 294, 299  
 Gower, A., 108(196), 131  
 Grabiell, C. E., 468(478a), 486  
 Grady, J. M., 212  
 Gragerov, I. P., 491(241), 567(241), 568 (241), 603  
 Graham, G. E., 329(149,150), 330(149, 150), 332(149,150), 334(150), 347, 377(160), 386(160), 395(160), 477  
 Graham, J. A., 667(129), 684  
 Graham, J. D., 108(193), 131  
 Gramaccioli, C. M., 491(192), 567(192), 602  
 Grammaticakis, P., 102(113), 129  
 Grant, G. A., 627(56), 641(56), 682  
 Grauer, F., 69(495), 610  
 Gray, C. W., 101(102b), 129  
 Gray, P., 170(22), 209, 220(26), 288  
 Graybeal, J. D., 8(13), 72  
 Graybill, B. M., 326(131,132), 346, 423(418), 428(418), 429(418), 484  
 Green, A. L., 492(278), 494(278), 533(278), 605  
 Green, G. F. H., 303(18), 343  
 Green, J., 234(104), 290  
 Green, M., 24(84), 32, 73  
 Greene, F., 179(51), 180(51), 210  
 Greenspan, F. P., 308(35,36), 343  
 Greenwood, H. H., 532(388), 607  
 Gregor, V., 285(430), 299  
 Gregory, J. T., 333(159), 347  
 Gregory, M. J., 364(111a), 476  
 Greizerstein, W., 491(45,46), 495(46), 498, 502(45,46), 503(46), 534(45), 535(45), 553(46), 599  
 Gresham, T. L., 333(159), 347  
 Grey, A., 34(115), 35(115), 74  
 Gribov, B. G., 431-433(436), 453(436), 458(436), 484  
 Griess, P., 614, 680  
 Griffin, C. E., 218(12), 249(193), 267(323), 268(324), 275(323), 287, 293, 296  
 Grimm, D., 303(20), 343  
 Grinter, R., 49-51, 75, 191(86), 210, 586(544), 611  
 Griswold, A. A., 107(187), 131, 176(44), 209, 316-319(83), 345, 388(235), 389(235), 409(337a), 479, 482  
 Grob, C. A., 516, 606

- Grob, J., 397(298), 398(298), 420(298),  
424(298), 444(298), 447(298), 481  
Grosheintz, J. M., 386(238), 388(238), 479  
Gross, J. M., 123(309,310), 124(317,318a),  
134, 135  
Grube, H., 491(118), 499-501(118),  
552(118), 601  
Gruber, W., 102(128), 129  
Grumetz, M., 151(52), 162  
Grunwald, E., 284(425), 299  
Grutznier, R., 310(47), 344  
Gudriniece, E., 314(67), 344, 412(369,376),  
413(369,376), 483  
Günthard, H. H., 38, 39(126), 74,  
167(12), 209  
Gulbaran, E., 261(272), 295  
Gulick, W. M., Jr., 64, 76, 123(311,312),  
134  
Gul'tyai, V. P., 353(41), 474  
Gundel, W., 275(370), 297  
Gunning, H. E., 219(19), 288  
Gupta, K. C., 251(203), 254(203), 293  
Gupta, S. M., 251(203), 254(203), 293  
Gurzynska, W., 463(471), 485  
Guser, S. S., 90(70), 128  
Gustorf, V., 245(172), 292  
Gutch, C. J. W., 240(130), 291  
Guttmann, A., 261(270), 295  
Gwinn, W. D., 32(105,106), 74, 106(181),  
131

## H

- Haberfield, P., 557(422), 608  
Haberman, J. P., 90(59), 127  
Hahn, C. S., 102(120), 129  
Haddadin, M. J., 268(326), 296  
Häflinger, O., 372(152), 376(152), 477  
Haeften, F. E. van, 563(464), 609  
Hage, S. M., 262(285), 295  
Haines, R. M., 671(135), 684  
Hake, A., 273(361), 297  
Hale, G. C., 651, 683  
Hall, G. E., 328(139), 346  
Hall, N. F., 629(63,64), 682  
Hall, R. H., 625(51), 644(106), 645(106),  
682, 683

- Hall, T. N., 90(59), 104(156), 127, 130,  
172(32), 209, 373(144), 477  
Halleux, A., 512(327), 513(327,331,332),  
520(351), 531(327,331,332,351),  
539(332), 544(327), 545(327), 606  
Halmann, M., 84, 126  
Ham, W., 272(354), 297  
Hamann, K., 417(389), 422(389), 483  
Hambly, A. N., 115, 133  
Hameka, H. F., 54(153), 75  
Hamel, E. E., 335(174), 336(174), 347  
Hamer, J., 86, 126, 270(335,336,339),  
278(390), 296, 298, 453(454), 470(454),  
485  
Hammett, L. P., 55(157), 75,  
284(426,427), 299, 534(406), 551(406),  
608  
Hammick, D. L., 118(271), 119(273,274),  
133, 207(137), 212, 377(165), 380(190),  
477, 478, 491(211), 521(211), 567(211),  
603  
Hammond, G. S., 326(131,132), 346,  
406(338), 423(418), 428(418), 429(418),  
482, 484, 490, 501(294), 504-506(294),  
517(346), 518(4), 520(294,346), 540(4),  
541(294), 545(294), 550(346), 551(346),  
552(294), 598, 605, 606  
Hammond, P. R., 521(377), 531(377), 607  
Hancock, C. K., 86(33), 101(104,105),  
104(157,158,162), 126, 129, 130  
Handa, J., 105(165), 131  
Handrick, G. R., 671(135), 684  
Hanford, W. E., 319(97), 345  
Hansen, R. L., 125(332), 135, 168(14),  
209  
Hanson, R., 388(239), 479  
Hanst, P. L., 218(4), 287  
Hanthal, H. G., 231(87), 290  
Hantzsch, A., 279(400), 280(400), 298,  
350, 351, 353, 354(32), 356(32), 358,  
362(1), 365, 366(32,113), 367(32),  
373(113,147), 374(32,113), 376(113),  
377(1,170), 380(1,32,33,194), 381(33),  
383(212), 386(32), 393(170), 394(170),  
397(170), 398(32), 399(33), 404(32),  
405(32), 407, 411(361), 412(339),  
413(339), 415, 416, 418(384), 419(384),  
420(194,384), 421(413), 422(194,384,413),

- Hantzsck, A. (*continued*)  
 423(384,415,416), 428(415,416), 438(384),  
 460(1,32,147,194,339,415), 462(170),  
 468, 471(1,33), 472(1), 473, 474, 476-  
 478, 482-484, 614, 618, 619, 642, 681
- Hanyu, Y., 161, 163
- Harcourt, R. D., 15(28), 24(78-80), 72,  
 73
- Hardwick, R., 181(61), 210, 354(67-69,  
 72,73,77), 355(77), 377(73), 379(73), 475
- Harres, L., 452(452), 485
- Harries, C., 623(40), 646, 649, 681
- Harriman, J. E., 28(94), 74, 125(329),  
 135
- Harris, R. K., 157(70), 163
- Harrison, W. A., 323(114), 345
- Hart, C. R., 526(383), 529-531(383),  
 571(383), 607
- Hartl, F., 273(360), 297
- Hasan, N. M., 579(521), 611
- Hashimota, M., 87(39), 127
- Hashimoto, S., 212
- Hass, H. B., 302, 316(81), 319(97),  
 333(159), 340(12), 341(191), 342-345,  
 347, 348, 350, 371(143), 386(231),  
 388(231), 389-391(143), 405(328),  
 417(5,388,393,397), 422(393,397),  
 426(5,388,393,397), 427(5,388,393),  
 428(328), 445(393), 449(5,388,393), 473,  
 477, 479, 482, 483
- Hassall, C. H., 310(45), 344
- Hassner, A., 313(58), 323(113), 344, 345,  
 389(248), 392(248), 479
- Hastings, S., 172(30), 173(30), 174, 209
- Haszeldine, R. N., 34(110), 74, 83(9), 126,  
 139(6,7), 144(6,7,26), 145(7), 146(6,7),  
 152(6,7), 153(7), 154(6,7), 161, 167(6),  
 205(127), 206, 209, 211, 212, 218(8,12),  
 222(37,38), 255(232), 265(311), 266(320),  
 269(331), 287, 288, 294, 296, 323(115),  
 345
- Hata, N., 65, 66(205,209), 67(205), 76
- Hathaway, C., 614(16), 616(16), 681
- Hausser, K. H., 21(55), 73
- Havinga, E., 151(46), 162, 200(102,104-  
 108), 211, 212, 253(225), 257(239),  
 294, 491, 566(273), 582(266), 583,  
 584(268,269,271-273,276), 585(274),  
 586, 604, 605
- Hawthorne, M. F., 248(189), 292,  
 306(30), 307(30), 326(131,132), 335,  
 343, 346, 347, 383(209), 385(209),  
 388(209), 389(209), 393(209), 404  
 (319,322), 405(319,322), 423(418), 428  
 (418), 429(418), 471(209), 478, 481, 484,  
 490, 496(284), 497(284), 502(284), 503  
 (284), 517(346), 518(4), 520(346), 530  
 (284), 540(4), 550(346), 551(346), 598,  
 605, 606
- Hayashi, R., 323(113), 345
- Hays, J. T., 260(250), 284(421), 294, 299
- Heald, J. S., 304(23), 343
- Heathcock, C., 110(206), 132, 323(113),  
 345
- Heath, R. L., 248(191), 292
- Heckert, D., 179-181(48), 210, 251(205),  
 293
- Hedges, R. M., 86(33), 101(104), 126, 129
- Heicklen, J., 265(309), 285(431), 296, 299
- Heidberg, J., 109(204), 132
- Heilbronner, E., 49-51, 75, 383(218), 479,  
 491(379), 531(379), 586(544), 607, 611
- Hein, G. E., 248(188), 292
- Heinke, J. L., 424(421), 484, 595,  
 596(568), 612, 620(29), 638(29), 681
- Heisle, R., 352(22), 389(22), 473
- Heitzer, H., 189, 206(133), 210, 212,  
 246(182), 261(275), 286(182), 292, 295
- Heller, G., 243(155), 247(185), 292,  
 469(482), 486
- Heller, P. H., 125(333), 135
- Helmkamp, R. W., 417(387), 422(387),  
 426(387), 427(387), 429(387), 445(387),  
 450(387), 483
- Hemminger, C. H., 385(226), 388(226),  
 395(226), 400(226), 479
- Hems, B. A., 570(501), 610
- Henderson, A. T., 15(34), 17(34), 19(34),  
 72
- Henglein, A., 218(9), 287
- Henley, R. V., 569(491), 610
- Henning, G. F., 651(111), 683
- Henrich, F., 233(94), 290
- Henry, L., 390(262), 480, 661(120), 683
- Henry, M. C., 268(327), 296

- Henry, R. A., 227(64), 228(64), 289, 625(52), 682
- Hepfinger, N. F., 249(193), 267(323), 268 (324), 275(323), 293, 296
- Heppler, L. G., 366(114), 373(114), 374(114), 476
- Hepp, E., 279(398,399,401), 298
- Hepp, P., 554(409), 608
- Heppolette, R. L., 491(124, 134-136, 141-143,287), 492(142), 495(287), 509 (124,135,136,141,142), 510(124,134-136,141-143,320), 511(136,141), 535(124), 536(135,142,287), 537(124,141), 540(124,134-136,141-143), 544(136), 554(143), 601, 605, 606
- Herber, J. F., 230(78), 289
- Herbert, S. A., 327(136), 346
- Herbison-Evans, D., 58(169), 75
- Herendeen, R., 125(342), 135
- Herre, W., 120(282), 134
- Herring, K. G., 629(67), 682
- Herrmann, P., 256(237), 294
- Hertel, E., 569(496), 610
- Hertog, H. J. den, 498(289), 581(526,527), 582(527), 605, 611
- Herz, E. v., 640(95), 683
- Herzberg, G., 8(11), 72
- Hess, H. D., 38(125), 74
- Hesse, E., 244(166), 292
- Heuser, G., 574(509), 610
- Hewett, J. V., 302(14), 343
- Heyden, A. van der, 491(273,276), 566(273), 584(273,276), 605
- Hibshman, H. J., 302(5), 342
- Hickford, R. S., 504(305), 550(305), 551(305), 605
- Hickinbottom, W. J., 223(44), 288
- Higaki, J. M., 304(23), 341(190), 343, 348
- Hiiro, A. M., 491(168), 507(168), 602
- Hijikata, K., 32(101), 74
- Hill, D. L., 491(159), 509(159), 511(159), 514(159), 515(159), 520(159), 533(159), 540(159), 550, 571(159), 576(159), 601
- Hill, H. B., 414(337), 483
- Hillers, S., 103(143), 125(334), 130, 135
- Hills, P. R., 220(25), 288
- Hilpert, S., 185, 186(74), 210
- Hinsberg, O., 614, 616, 680
- Hiraoka, H., 354(73), 377(73), 379(73), 475
- Hirschloff, E., 170(23), 209
- Hirst, D. M., 24(85), 25(85), 73
- Hirst, E. L., 667(127), 683
- Hirst, J., 491(23,25-31), 492(26), 497(30), 500(23), 501(30), 504(30), 505(23), 508(23), 509(25,28), 511(23), 512(27), 513(27), 514(23,27), 516(29), 517(29), 529(30), 531(27), 534(28), 535(28), 538 (25), 541(25,29), 545(29,30), 546(30), 547(23), 549(29), 550(29), 552(30), 578(30), 598, 599
- Hitchings, T. R., 271(350), 297
- Hixon, R., 226(60), 289
- Hiyama, H., 235(106), 290
- Ho, K. C., 491(159,160), 508(160), 509 (159,160), 511(159,160), 514(159,160), 515(159,160), 520(159,160), 533(159,160), 540(159,160), 542(160), 550(159,160), 571(159), 576(159), 601
- Hochstrasser, R. M., 120(279,289), 134
- Hockenberger, L., 648(108), 683
- Hodge, E. B., 302(1,2,9), 342, 343, 352, 381(27), 382(27), 400(27), 401(27), 474
- Hodgeson, J. A., 23(71), 32(71), 73
- Hodgkin, D. C., 15(31), 72, 252(216), 293
- Hodgson, H. H., 561(452), 609
- Hodgson, W., 205(126), 211
- Hodos, M., 360(85a), 475
- Höchtlen, A., 429(433), 462(433), 484
- Höhn, R., 256(237), 294
- Hoeche, K., 431(446), 485
- Hoek, T. C. van, 223(44), 288
- Hoekstra, S. E., 151(46), 162, 253(225), 294
- Hofer, P., 308(39), 309(39), 343
- Hoffman, A., 205(126), 211
- Hoffman, F., 37(120), 74, 305(28), 307(28), 343
- Hoffmann, A. K., 15(34), 17(34), 19(34), 72
- Hoffmann, H., 263(291), 277(382), 295, 298
- Hoffmann, R., 7(8), 25(8), 71
- Hoffner, K., 574(510), 610
- Hoffsommer, J. C., 340(185), 348



- Hofman, W., 38(122), 74, 106(184), 131, 363(97), 475
- Hoganson, E., 176(44,45), 177(44,46), 178(46), 209, 210, 388(234,235), 389(234,235), 479
- Hoijsink, G. J., 59(188), 76
- Hokama, T., 314(61), 316(82), 318(82), 344, 345, 451(451), 485
- Holden, A. N., 120(292), 134
- Holder, B. E., 266(318), 296
- Holdermann, K., 623(43), 681
- Holeci, I., 83(12), 126
- Holland, D. O., 233(97), 290
- Holleck, 139(13), 151(51), 161, 162, 558(432), 608
- Holleman, A. F., 350(9), 351, 353, 356 (63), 397(292), 412(54), 413, 463(475), 464(475), 473, 474, 481, 486, 542(394), 563(464), 565(468), 592(561), 608, 609, 612
- Holliday, R. E., 270(335), 296
- Hollis, D. P., 156, 163
- Holly, S., 91(83), 128
- Holmes, R. R., 151(47), 162, 253(224), 254(226), 293, 294
- Hones, R. Z., 116(263), 133
- Horner, L., 263(291), 277(382), 295, 298, 648(108), 683
- Hornman, I., 491(227, 228), 521(227, 228), 603
- Horsfield, A., 22(62), 73
- Horton, W. J., 640(97), 683
- Horvath, G., 101, 129
- Houben, J., 225(53), 289
- Howe, A. P., 302(11), 343, 386(231), 388(231), 479
- Howell, W. C., 327(135), 346
- Hoyt, J. M., 218(11), 287
- Hsue, G., 119(277), 134
- Huber, H., 678(170,171), 684
- Huber, M. I., 391(272,273), 480
- Hubner, R., 241(145), 242(146,149), 245(173), 291, 292
- Hudson, A., 182(65), 210
- Hudson, R. F., 490, 533, 550(9), 552(9), 554(9), 598
- Hübner, H., 256(237), 294
- Hückel, W., 321(107), 327(137), 342(137), 345, 346
- Hughes, E. D., 224(49), 289, 491(21), 511(21), 539(21), 546(396), 598, 608, 622(33), 681
- Hughes, E. W., 674(160), 684
- Huisgen, R., 254(229), 294, 490, 554(411), 555(414), 565(411), 596(578), 598, 608, 612
- Huitric, A. C., 38(124), 74, 107(189), 131, 363(98,99), 475
- Hundson, A., 124(319), 135
- Hunt, J. S., 303(18), 343
- Hunter, L., 405(325), 481
- Hunter, W. T., 388(239), 479
- Huntley, E. B., 219(17), 288
- Hurd, C. D., 314(62), 321(106), 344, 345
- Hurley, R., 48(145), 75, 174(37), 183(73), 209, 210, 212, 213
- Hurtig, G., 271(343), 297
- Hutchison, C. A., 121(294), 134
- Hutley, B. C., 504(306), 605
- Hutton, H. M., 109(199), 131
- Hyashi, R., 111(220), 132
- Hylin, J. W., 333(160), 347

## I

- Ibañez, L. C., 324(121), 346, 363(94), 475
- Ibne-Rasa, K. M., 151(50), 162, 226-228 (61), 247(184), 264(302), 289, 292, 295
- Ibragimov, A. P., 90(65), 127
- Iffland, D. C., 235(112), 238(123,125), 290, 291, 304, 305(26,27), 306, 325(126), 326(126), 329(144), 343, 346, 352(18), 429(434), 473, 484
- I'Haya, Y., 45, 75, 96, 128
- Illuminati, G., 490, 581, 582(14,532), 598, 611
- Il'yasov, A. V., 124(321), 135
- Ingebrectsen, K., 260(254), 294
- Ingold, C. K., 224(49), 283(420), 289, 298, 490, 491(21), 511(21), 539(21), 552(3), 598
- Ioffe, S. L., 453(458), 456(458), 457(458), 485
- Iogansen, A. V., 84(23,28), 91(81), 113 (81), 126, 128

Isacescu, D. A., 360(84), 379(84), 381(84), 382(84), 392(275), 400(84), 401(84), 402(84,308), 405(84), 406(84), 417(84,275), 421(275), 422(275), 445(308), 448(84), 450(84,308), 452(84), 462(275), 463(275), 465(275), 475, 480, 481  
 Isaenkova, M. A., 399(302), 481  
 Iselin, B., 386(237), 388(237), 479  
 Ishidate, M., 560(448), 609  
 Ishikawa, N., 514(329), 606  
 Ishitani, A., 64, 76, 105(172), 123(172), 131  
 Isik, H., 420(412), 422(412), 443(412), 484  
 Iskander, Y., 102(115), 129  
 Isler, O., 417(392), 422(392), 445(392), 449(392), 450(392), 483  
 Issidorides, C. H., 268(326), 296  
 Ito, H., 292  
 Ito, M., 65, 66(205), 67(205), 76, 229(73), 289  
 Itoch, M., 106(177), 125(177), 131  
 Ivanov, A. I., 84(22), 126, 371(153), 373(145), 374(145), 375(153), 383(206), 418(402), 435(402,449), 460(464), 477, 478, 483, 485  
 Ivanov, A. V., 491(246,253-255), 566(253-255), 568(246), 604  
 Ivanova, V. M., 491(248), 566(248), 568(248), 604  
 Ivett, R. W., 472(490), 486  
 Izmail'ski, V. A., 102(119), 129  
 Izrailevich, E. A., 558(428), 608  
 Izzo, P. T., 563(463), 564(463), 609

**J**

Jache, A. W., 23(71), 32(71), 73  
 Jackson, C. L., 377(162-164), 477  
 Jackson, P. E., 269(331), 296  
 Jacquignon, P., 90(61), 127  
 Jaffe, H., 65, 67(206), 68, 76, 91(84), 92(84), 128, 147-149(35), 153, 162, 163, 534(393), 537(393), 551(393), 608  
 James, A. T., 224(49), 289  
 James, D. S., 424(420), 447(420), 448(420), 484  
 Jander, J., 139(6), 144(6,26), 146(6), 152(6), 154(6), 161, 222(37), 288

Jannakoudakis, D., 104(159), 130  
 Jansen, E. G., 125(335), 135  
 Jansen, J. E., 333(159), 347  
 Janusonis, G. A., 109(204), 132  
 Janzen, E. G., 58(176), 76, 276(377), 298, 399(305), 402(305,312,315), 430(312,315), 481, 558(427), 608  
 Jarrett, H. S., 21(53), 73, 121(295), 134  
 Jart, A., 90(64), 127  
 Jaubert, G. F., 280(404), 298  
 Jaxon-Deelman, J., 353(34), 354(34), 356(34), 366(34), 373(34), 474  
 Jeacocke, G. J., 145(30), 146(30), 162  
 Jeffery, G. H., 675(168), 678(168), 684  
 Jeffrey, G. A., 23(72), 73  
 Jelagin, S., 267(321), 296  
 Jencks, W. P., 502(298), 507(298), 524(298), 527(298), 573(298,507), 605, 610  
 Jenner, E. L., 640(97), 667(128), 683  
 Jibril, A. O., 582(528), 611  
 Jobling, E., 673(142), 684  
 Johannes, W., 282(414), 298  
 Johnson, A. E., 331(157), 347  
 Johnson, A. W., 278(391), 298  
 Johnson, B. G. H., 102(111), 129  
 Johnson, F., 363(95), 475  
 Johnson, K., 386(229), 388(229), 438(229), 439(229), 447(229), 460(229), 479  
 Johnson, R., 201(112), 211  
 Johnson, R. A., 220(25), 288  
 Johnson, R. D., 106(181), 131  
 Johnson, R. M., 587(545), 611  
 Jonathan, N., 69, 70(219,220), 77, 671(134), 684  
 Jones, E., 167(10), 209  
 Jones, E. R. H., 94(91), 111(219), 128, 132, 302, 303(16), 306(16), 307(16), 323(16, 114), 330(16), 343, 345  
 Jones, G. T., 224(49), 289  
 Jones, J., 111(218), 132  
 Jones, J. K. N., 667(127), 683  
 Jones, L. A., 104(162), 130  
 Jones, L. W., 463(474), 464(474), 486  
 Jones, P., 367(126), 368(126), 476  
 Jones, R. N., 673(149), 684  
 Jones, W. J., 242(148), 291, 309(42), 310(42), 334(170), 343, 347

- Jones, W. M., 102(121), 116(264), 129, 133, 342(195), 348, 424(420a), 484
- Jongh, R. O. de, 491(265,266,268,272), 582(266), 583(266,268,272), 584(265,268,272), 604, 605
- Jorgenson, M., 168(18), 180(53), 209, 210
- Joshi, S. S., 505(310), 506(310), 564(310), 605
- Jouwermans, C., 498(289), 581(527), 582(527), 605, 611
- Jürgens, B., 389(249,250), 391(249), 392(249,250), 393(250), 395(249), 407(249), 465(249), 479
- Juillard, 279(402), 298
- Jun, M. J., 245(172), 292
- Junell, J., 368(123), 476
- Junell, R., 353(37), 365, 366(37), 370(37), 371(37), 373(130,132), 375(132), 474, 476
- Jung, F., 251(207), 293
- K**
- Kääriäinen, L., 491(177), 520(177), 581(177), 602
- Kabasakalian, P., 221(31,33), 222(31,33), 253(219), 288, 293
- Kahr, K., 241(142), 291
- Kaiser, L. E., 552(400), 608
- Kai-Yan, W., 491(152), 508(152), 509(152), 511(152), 534(152), 540(152), 542(152), 601
- Kalabina, A. V., 102(112), 129
- Kalberer, F., 505(311), 534(311), 606
- Kalle and Co., 244(162), 292
- Kamentani, T., 370(140), 476
- Kametani, T., 322(108), 345
- Kaminskii, A. Ya., 377(172), 477, 491(236,244,245,250-252,256), 560(236,245,250-252), 566(244), 568(236,244,245), 603, 604
- Kaminsky, D., 518(350), 606
- Kamlet, M. J., 89, 90(56), 105(168), 127, 131, 340(185), 348, 366(118), 373(118), 374(118,148a), 375(118), 376(118), 476
- Kandel, R. J., 31, 34(95), 74, 170(21), 209
- Kaneko, C., 183(72), 210, 212
- Kaplan, L. A., 89, 127
- Kaplan, M., 124(320), 135
- Kaplan, R. B., 319(91), 336-339, 345, 347, 402(311), 426(425), 427(425), 481, 484
- Kapoor, R. P., 251(203), 254(203), 293
- Karabatsos, G. J., 108(193), 131, 156, 157(69), 163
- Karelitz, R., 512(317), 606
- Karle, I. L., 32(104), 74
- Karle, J., 32(104), 74
- Karplus, M., 55, 59, 61, 75, 76
- Karrer, P., 175(39), 209, 246(178), 292
- Kasha, M., 168, 209
- Kastening, B., 105(170), 131
- Kastler, A., 671(133), 684
- Kato, H., 24(77), 26(77), 29-31(77), 73
- Katritzky, A. R., 65, 70, 76, 77, 88(46a, 46b), 127
- Kauffmann, T., 234(104), 262(285), 290, 295
- Kaufman, J. V. R., 461(468), 485
- Kaufmann, M., 491(35,38), 501(35), 522(35), 523(35), 525(38), 528(35), 529(35, 38), 530(35), 599
- Kawata, M., 560(440), 609
- Kazarnovskii, S. N., 15(37), 72
- Keefer, R. M., 116, 117(268), 119(268), 120(268,278), 133, 134
- Keen, N., 32(100), 74
- Kehrmann, F., 262(279), 295
- Keller-Schierlein, W., 328(139), 346
- Kellman, A., 168(19), 209
- Kempf, R., 186(77), 210, 246(179), 292
- Kemula, W., 104(154), 105, 130, 131, 263(287), 295, 353(53), 356(53), 366(53), 373(53), 383(53,207,208), 473(53), 474, 478
- Kendall, F. H., 513(328), 514, 606
- Kent, B. A., 590(553), 611
- Kenyon, J., 233(97), 273(359), 290, 297
- Kerber, R., 190(84), 210, 360(85a,86a), 426(424,427), 427(424), 475, 484
- Kerimova, M. M., 228(65), 289
- Kerr, S., 125(342), 135
- Kessler, H., 84, 126
- Ketelaar, J. A. A., 11(19), 72, 557(420), 558(420), 608
- Keussler, V. V., 149(45), 150(45), 162, 253(221), 293
- Keynon, W. O., 261(263), 294

- Khaletskii, A. M., 579(522), 611  
 Khan, N. R., 504(306), 605  
 Kharasch, M. S., 220(28), 271(28), 288  
 Khidekel, M. L., 15(38), 72  
 Khmel'nitskii, L. I., 378(181,182), 395(181, 182,285,286), 396(181,286), 478, 480  
 Kiefer, R. M., 520(355), 607  
 Kiefer, W. F., 510(321), 524(321), 606  
 Kierstead, R. W., 146(33), 160(33b), 162  
 Kiese, M., 251(208), 293  
 Kikuchi, C., 121(296), 134  
 Kimball, G. E., 5(4), 6(4), 71  
 Kimura, M., 507(313), 560(313,438,440, 446,447), 606, 609  
 Kindig, J., 614(16), 616(16), 681  
 King, D., 508(318), 554(318), 606  
 King, I. R., 56(162), 75  
 King, T. J., 560(441), 609  
 Kingsbury, C. A., 503(303), 508(303), 510 (303), 511(303), 514(303), 521(303), 551-553(303), 557(422), 605, 608  
 Kinkade, J. W., Jr., 121(299), 134  
 Kinney, C. R., 461(467), 485  
 Kinugasa, T., 87, 127  
 Kipping, F. S., 411(353), 482  
 Kirby, A. J., 502(298), 507(298), 524(298), 527(298), 573(298,507), 605, 610  
 Kirby, G. W., 56(162), 75  
 Kirkien-Konasiewicz, A., 573(504,505), 610  
 Kirkwood, M. W., 622(33), 643(103), 644 (104), 645(103), 681, 683  
 Kirmse, W., 251(204), 293, 648, 683  
 Kirpal, A., 633, 682  
 Kiser, R. W., 10(17), 13(17), 72  
 Kiss, A. I., 101, 129  
 Kiss, J., 322(112), 345  
 Kissel, H., 377(170), 393(170), 394(170), 397(170), 462(170), 464, 477  
 Kissel, J., 463(472), 464, 485  
 Kissinger, L. W., 102(132), 112(230,231), 113(237), 114(230,231), 130, 132, 237 (120), 291, 315(73), 339(181), 344, 348, 633(71), 682  
 Kitaev, Y. P., 124(321), 135  
 Kitano, H., 332(164), 333(164), 347  
 Kitasato, Z., 465(478), 486  
 Kittel, C., 120(292), 134  
 Kiuttu, M., 491(176), 507(176), 509(176), 536(176), 549(176), 602  
 Kivlevich, D., 331(156), 332(156), 347  
 Kiyanskaya, L., 180(54), 210  
 Klager, K., 311(52), 344  
 Klages, F., 352(22), 389(22), 473  
 Klahre, G., 277(382), 298  
 Klamann, D., 230(80), 232(89), 290, 322 (109), 345  
 Klaube, E., 272(353), 297  
 Klein, J. R., 614(16), 616(16), 681  
 Kleinberg, J., 262(286), 295  
 Klimova, A. I., 90(75), 128  
 Klimova, V. A., 353(38), 354(55), 356(55), 366(38,55), 372(55), 373(38,55), 393(276), 399(276), 443(276), 471(276), 472(38), 474, 480  
 Klinck, R. E., 110(205), 132  
 Klobbie, E. A., 614(4), 615, 637(83,86,89), 638(93), 639(83,86), 640(97), 680, 682, 683  
 Klykova, L. V., 412-414(375), 483  
 Klyne, W., 21(57), 73  
 Knap, A., 204(124), 211  
 Kneip, A., 308(36), 343  
 Knöffler, 660  
 Knoll, N., 222(36), 288  
 Knop, A., 161(78), 163, 204(124), 211, 252(213), 293  
 Knorr, L., 258(241), 294  
 Knowles, J. R., 511(323), 520(323), 550 (323), 551(323), 606  
 Knox, L. H., 596(576,577), 612  
 Knudsen, E. S., 106(179), 131  
 Knunyants, I. L., 231(83), 237(118), 240 (136), 248(191), 270(340), 271(344), 284 (118), 285(118), 290-292, 296, 297, 374 (149), 378(184a), 477, 478  
 Knupfer, H., 277(386), 298  
 Knutson, D., 213, 491(54,56), 510(54), 511 (54), 530(56), 534(54), 599  
 Kobayashi, S., 245(170), 292  
 Kobzina, J. W., 102(121), 129, 342(195), 348  
 Kochetkov, N. K., 435(448), 485  
 Kögl, F., 276(376), 297  
 König, H., 556(417), 608  
 Koenyves, I., 111(222), 132

- Koerner, E., 245(172), 292
- Kohler, E. P., 341(193), 348, 352(26), 354 (65), 362(65), 378(65), 386(65), 389(65), 398-401(65), 417(65), 422(65), 429(438), 430, 431(441), 433(26,437,438), 434(441, 443), 435(65,437), 474, 484, 485
- Kohlrausch, K. W. F., 670(131), 671, 684
- Kohn, L., 302(14), 343
- Kohn, M., 569(495), 610
- Kohvakka, E., 491(178), 520(178), 567 (178), 568(178), 602
- Kojima, M., 42(133), 43(133), 45(133), 75, 95(94), 96(94,97), 128, 168(13), 209
- Kolthoff, I. M., 263(289), 295
- Kolyer, J. M., 261(262), 294
- Kon, G. A. R., 362(88), 475
- Konel'skaya, V. N., 102(118), 129, 153 (61), 163
- Konig, E., 256(236), 294
- Konowalow, M. I., 351, 377(13,159), 380 (13,159), 400(13), 401, 460(463), 471, 473, 477, 485
- Konstantinov, Yu. S., 231(83), 290
- Koppe, M., 390(261), 391(261), 480
- Koral, M., 304(25), 306(25), 343
- Korchemnaya, T. B., 353(38-42), 354(39, 55), 356(39,42,55), 364(40,42), 365(40), 366(38,39,42,55), 367(139), 372(55), 373 (38-40,55), 376(158), 472(38), 474, 476, 477
- Korcynski, A., 416(385), 483
- Kornblum, N., 82(6), 83(6), 90(6), 126, 190(83,84), 210, 242(148), 291, 302(15), 309(41,42), 310(42), 325(125-127,130), 326(125,126,134), 327(125,127,134,136), 328(15,127), 329, 330(149-152,155), 331 (151), 332(149-152), 333(151,166), 334 (150,166,170), 343, 346, 347, 352(18,19, 23), 366(116), 373(116), 374(116), 376 (116), 377(160), 385(222), 386(160,222), 389(222), 390(222), 395(160), 417, 418-420(23), 422-424(23), 426(424,426-428), 427(424,426), 428(430), 429, 435-437 (23), 438(222), 440, 441(222), 447(23), 451, 459(23), 473, 476, 477, 479, 484
- Korolev, A. I., 228(67), 260(67), 289
- Koroleva, I. N., 262(282), 295
- Korsakova, I. S., 340(184), 348, 378(178), 380(178), 383(178), 397(288,289), 436(178), 478, 480, 481
- Kortüm, G., 34(108), 74, 125(337), 135, 673(146), 684
- Koryrev, Yu. M., 248(191), 292
- Koser, W., 230(80), 290, 322(109), 345
- Kosinski, M., 236, 237(115), 291
- Kosower, E. M., 520(360), 607
- Kosvrev, Yu. M., 286(434), 299
- Kotoucek, M., 272(355), 273(355), 297
- Koubak, E., 151(50), 162, 247(184), 292
- Kovacs, J., 322(112), 345
- Kovaliv, Yu. D., 153(60), 163
- Kowalsky, A. G., 121(294), 134
- Kozyrev, B. M., 121(300), 134
- Kraaijeveld, A., 257(239), 294
- Kraljic, I., 266(319), 296
- Krasnosel'skaya, E. A., 228(65), 289
- Krasovitskii, B. M., 491(259), 505(259), 604
- Kratzer, J., 232(89), 290
- Kraus, A., 226(63), 289
- Krauss, R. C., 579(520), 580(520), 611
- Kremers, E., 226(60), 289
- Krestschmann, K., 228(66,70), 289
- Kresze, G., 270(338), 296
- Kretov, A. E., 235(111), 290
- Kreuz, K. L., 88(49), 127, 389(247), 390 (247), 406-408(333), 479, 482
- Kristjanson, A. M., 493(280), 513(280), 514(280), 605
- Kröhnke, F., 197(99), 211, 277(383), 278 (383,390), 298
- Kröhnke, G., 197(99), 211, 277(383), 278 (383), 298
- Kronenberg, M., 200(108), 211, 212, 491 (273,276), 566(273), 584(273,276), 605
- Kross, R. D., 85, 86(31), 89, 126
- Kroto, H. W., 148(41), 162
- Kruger, G., 491(147), 492(147), 509(147), 510(147), 536(147), 540(147), 601
- Kruglyak, Y. L., 324(122), 346
- Kruse, C. W., 512(326), 513(326), 552 (326), 565(326), 606
- Kruse, J. M., 219(17), 288

Kubli, A., 378(177), 380(177), 381(177),  
460(177), 478  
Kubota, T., 22(63,64), 23, 65, 66(208),  
67(207), 68, 73, 76  
Kuchenbecker, A., 614(12), 616(12), 681  
Kuhn, M., 114, 133  
Kuhn, R., 264(300), 295, 328(143), 346,  
352(16), 353(16), 473  
Kuhn, S. S., 159(74), 163  
Kuhnel, M., 318(89), 345  
Kuindshi, B., 354(79), 475  
Kumagi, H., 242(151), 291  
Kumai, T., 377(166), 477, 521(373), 567  
(373), 607  
Kumler, W. D., 88(48), 90(48), 127, 640  
(98), 641(100), 643, 673(156), 675, 684  
Kunder, H., 225(55), 289  
Kunkle, A. C., 23(71), 32(71), 73  
Kunovskaya, D. M., 230(82), 290  
Kuntz, I., 491(103), 503(103), 504(103),  
524(103), 525(103), 600  
Kupchan, S. M., 325(129), 346  
Kurihara, Y., 229(77), 289  
Kuroda, H., 119(276), 133  
Kurreck, H., 125(331), 135  
Kuwata, K., 64(200), 76, 105(172), 123  
(172), 131  
Kvitko, I. Ya., 223(47), 288  
Kvitko, S. M., 116(262), 133

**L**

Labes, M. M., 228(72), 289  
Labhart, H., 40(129), 42(129,134), 44(129,  
134), 46(129), 47, 48(129), 51-53(129),  
75  
Laboratoires Lumiere et Institut  
Merieux, 250(202), 293  
Lacher, J. R., 218(13), 231(88), 287, 290  
Lachman, A., 261(269), 295, 614, 615,  
624(45), 681  
Lagercrantz, C., 122(303,304), 124(328),  
134, 135, 186(64), 210, 587(547), 611  
Lagodzinskaya, G. V., 418(398), 453(398,  
458), 454(398), 455(398), 456(398,458),  
457(458), 458(398), 483, 485  
Lagrange, C. G., 90(58), 127  
Lagutina, Z. N., 274(364), 297

Lahiri, S. C., 105(164), 130  
Laizane, Z., 314(68), 344  
Lakritz, J., 368(122), 370(122), 476  
Lam, K. B., 491(158), 540(158), 601  
La Manna, A., 155(66), 163  
Lambert, J. B., 57, 58(166), 75, 110(209),  
132, 321(107), 345  
Lamberton, A. H., 623(41), 624(46), 633,  
681, 682  
Lamchen, M., 352(24), 453(24), 470(24),  
473  
LaMer, V. K., 353(28-30), 356(29,30), 364  
(28), 366(28), 368(28), 372(28), 373(28),  
375(30), 473(28-30), 474  
Lamm, B., 531(378), 607  
Lampe, F. W., 266(317), 296  
Landsteiner, K., 622(36), 681  
Lang, F. M., 673(148), 684  
Lang, W., 228(69), 289  
Langen, J. O. M. van, 493(281), 505(281),  
539(281), 541(281), 605  
Langkamerer, C. M., 244(163), 260(163),  
292  
Langley, W. D., 241(143), 291  
Langowski, J. J., 104(161), 130  
Lantseva, L. T., 378(184a), 478  
Lantzka, I. R., 491(143), 510(143), 540  
(143), 554(143), 601  
Lanzoni, M., 220(24), 288  
Laptev, N. G., 264(305), 296  
Lapworth, A., 276(371), 297, 411(353),  
482  
Larkin, J., 313(58), 344, 389(248), 392  
(248), 479  
Larsen, A. C., 674(161), 684  
Larson, H. O., 111(223), 132, 301, 304  
(23), 315(71), 329(149,150), 330(149,  
150), 332(149,150), 334(150,170), 341  
(190), 343, 344, 347, 348, 421(414),  
436(414), 438(414), 442(414), 444(414),  
452(414), 484  
Latimer, W. M., 263(288), 295  
Laubenheimer, A., 561(451), 609  
Lauer, W. M., 244(163), 260(163), 292  
Lauro, C. G., 264(302), 295  
Lautenschlager, F., 676(169), 684  
Lauterback, G., 256(237), 294  
Lauterbur, P. C., 57, 75

- Lavrushin, V. F., 102(135), 130  
 Layloff, T., 124(314), 135  
 Layne, W. S., 153(63,64), 163  
 Lazdins, O., 614(16), 616(16), 681  
 Leach, W. A., 491(102), 501(102), 524  
 (102), 525(102), 600  
 Leahy, G. D., 491(121,137), 494(121), 510  
 (121,137), 511(121), 540(121,137), 544  
 (121), 546(121), 601  
 Leandri, G., 517, 564(340,345), 576(345),  
 577(343), 579(344), 580(344), 606  
 Learn, D. B., 614(15), 616(15), 628(15),  
 681  
 Leavitt, J. J., 673(150), 684  
 Lebedev, O. L., 15(37,38), 72  
 Lebedev, O. V., 378(181,182), 395(181,  
 182,285,286), 396(181,286), 478, 480  
 Lecomte, J., 88(48), 90(48), 127  
 L'Ecuyer, P., 594, 612  
 Lee, H. K., 102(120), 129  
 Lefebvre, R., 7(10), 71(225), 72, 77  
 Lefebvre-Brion, H., 8, 10, 72  
 Le Fevre, R. J. W., 144(25), 145(25), 153  
 (58), 162, 163, 260(246), 294, 569(490),  
 610  
 LeGoff, R., 24(83), 73  
 Leicester, J., 675(168), 678(168), 684  
 Leighton, P., 172(32), 186(76), 189(76),  
 209, 210  
 Leighton, R. A., 246(180), 292  
 Leipprand, F., 232(93), 290  
 Leitch, L. C., 385(224), 479  
 Lemaire, H., 15(36,42), 16(42), 17(36,42,  
 44), 18(36,42,46,49), 18(36,42,44), 20(48-  
 50), 21(42,44,48,50,56,61), 22(48), 68(48),  
 69(48), 70(42), 72, 73, 261(273), 295, 304  
 (23), 343  
 Lemmer, F., 469(484), 486  
 Lenz, G., 176(44), 177(44), 209, 388(235),  
 389(235), 479  
 Leopold Casella and Co., 225(54), 289  
 Lepley, A. R., 118(270), 133  
 Lerner, O. M., 328(141), 333(141), 346,  
 362(90), 475  
 Leston, G., 325(128), 327(128), 328(128),  
 335(175), 346, 347, 404(323), 481  
 Letsinger, R., 200(109), 210(109,110), 202,  
 211, 583(539,540), 584(539,540,542),  
 586, 611  
 Leuchs, F., 242(147), 291  
 Levand, O., 111(223), 132, 304(23), 315  
 (70), 334(170), 343, 344, 347, 421(414),  
 436(414), 438(414), 442(414), 444(414),  
 452(414), 484  
 Levchenko, N. F., 491(258-261,263), 505  
 (258-261,263), 604  
 Levering, D. R., 88(48), 90(48), 127, 145  
 (28), 162, 335(173), 337, 347, 671(136),  
 684  
 Levinstein, H., 397(296), 398(296), 400  
 (296), 401(296), 424(296), 481  
 Levitsky, H., 90(68), 128  
 Levy, D. H., 64(198), 76, 124(315), 135,  
 160, 163  
 Levy, N., 319(92-96), 345, 390(267), 391  
 (267), 480  
 Lewis, E. S., 367(135,136), 476, 515(334),  
 606  
 Lewis, I. C., 59, 63(184), 76, 534(405),  
 551(405), 608  
 Ley, D. L., 414(381), 483  
 Ley, H., 366(113), 373(113), 374(113), 376  
 (113), 476  
 Ley, R. V., 517(347), 606  
 Libers, R., 339, 348, 363(105), 386(105),  
 391(105), 392(105), 394(105), 476  
 Lichtenthaler, F. W., 108(192,194), 131  
 Lichtin, N., 329(144), 346, 352(18), 473  
 Lieber, E., 88(48), 90(48), 127, 145(28),  
 162, 624(47), 671(136), 682, 684  
 Lieber, L., 673(153), 684  
 Lieberman, S. V., 445(450), 449(450), 450  
 (450), 451(450), 485  
 Liegalve, A., 103(143), 130  
 Lieste, J., 233(98), 290  
 Limpricht, J., 223(48), 289  
 Lin, C. C., 32(101), 74  
 Lindler, H., 417(392), 422(392), 445(392),  
 449(392), 450(392), 483  
 Lindley, C., 623(41), 681  
 Lingane, J. J., 263(289), 295  
 Linnett, J. W., 15, 24(84,85), 25(85), 32,  
 72, 73, 253(220), 293  
 Linstead, R. P., 653

Linton, E. P., 22(65), 73  
 Liotta, C. L., 512(317), 606  
 Lipina, E. S., 84(27), 126, 362(89), 475  
 Lipp, P., 321, 345  
 Lipparini, L., 279(396), 298  
 Lippert, E., 47, 75  
 Lippincott, S. B., 371(143), 389-391(143), 477  
 Liptay, W., 47, 75, 120(287), 134, 558 (434), 608  
 Litovchenko, G. D., 84(23,28), 91(81), 113(81), 126, 128  
 Litvinenko, L. M., 491, 505(257-264), 551 (257), 604  
 Liversedge, F., 151(48), 152(55), 162, 163  
 Liversis, M., 491(120,128,136,137,139,144, 148,154), 492(139), 493(120,144), 495 (128), 508(120,128,139,144), 509(120,128, 136,139,144), 510(128,136,137,144), 511 (120,128,136,144), 520(128), 534(144), 536(120,139), 540(120,128,136,137,139, 144,148,154), 544(128,136), 564(139), 581(154), 601  
 Llewellyn, F. J., 618(25), 681  
 Lloyd, D., 383(219), 415(219), 479  
 Lobry de Bruyn, C. A., 555(416), 561 (450), 562(462), 608, 609  
 Locher, J., 371(141,142), 385(141), 390 (141,142), 391(142), 476  
 Locke, A. W., 371(140a), 390(140a), 391 (140a), 476  
 Lode, A., 412(366,367), 413(366,367), 460 (366), 461(366), 482  
 Loeffler, K. O., 379(185), 478  
 Löwdin, P. O., 28(92,93), 74  
 Loewe, L., 420(412), 422(412), 443(412), 484  
 Long, A. G., 303(18), 343, 570(501), 610  
 Long, G., 558(429), 575(429), 577(429), 608  
 Long, L. M., 307, 314(33), 343  
 Longridge, J. L., 367(126), 368(126), 476  
 Longuet-Higgins, H. C., 124(319), 135, 182(65), 210  
 Looney, C. E., 155, 156, 163  
 Loos, K. R., 38(125,126), 39(126), 74, 167(12), 209  
 Losanitsch, S. M., 405(326), 481

Lossing, F. P., 31(98), 74  
 Lothrup, W. C., 671(135), 684  
 Lotspeich, F. J., 304(25), 306(25), 343  
 Loudon, J. D., 557(424), 558(424), 562 (460), 564(424), 565(460), 608, 609  
 Loughrom, E. D., 112(231), 114(231), 132  
 Louwrier-de Wal, J., 597(585), 612  
 Love, J. A., 335(174), 336(174), 347  
 Love, R. F., 88(49), 127, 406-408(333), 482  
 Lower, S. K., 120(279,289), 134  
 Lown, J. W., 238(126), 291  
 Lowry, T. M., 315(69), 344, 409(337), 411(337,354-360), 482  
 Lucas, A., 406(331), 407(331), 482  
 Luckhurst, G. R., 21(51), 73  
 Lucy, F., 186(76), 189(76), 210, 246(180), 292  
 Ludwig, P., 37(121), 38(121), 62(121), 74, 121(302), 134  
 Lührmann, J., 569(496), 610  
 Luke, W. K. H., 421(414), 436(414), 438 (414), 442(414), 444(414), 452(414), 484  
 Luk'yanchuk, S. V., 101(106), 129  
 Luk'yanova, L. V., 410(343), 482  
 Lund, E., 155(65), 163  
 Lunn, W. H., 82(11), 83, 126  
 Lutskü, A. E., 153(61), 163  
 Lüttke, W., 114(242), 133, 138(1), 139, 140(1,11), 141(1), 142(11,20), 146, 147 (1), 149(45), 150(45), 161, 162, 211, 253 (221), 254(227), 284(422), 293, 294, 299  
 Lutz, P. G., 491(120,128,136,144), 493 (120,144), 495(128), 508(120,128,144), 509(120,128,136,144), 510(128,136,144), 511(120,128,136,144), 520(128), 534 (144), 536(120), 540(120,128,136,144), 544(128,136), 601  
 L'vovich, I. G., 491(247), 558(247), 562 (247), 564(247), 568(247), 604  
 Lyttle, D. A., 315(72), 344

M

McAlonie, G. E., 93(89), 104(89), 128  
 Macaluso, A., 270(339), 278(390), 296, 298, 453(454), 470(454), 485  
 McBee, E. T., 386(233), 388(233), 479



- Macbeth, A. K., 356(61), 360(61), 474
- McCain, J., 200(109), 201(109,110), 211
- McCallum, K. S., 90(62), 111(227), 127, 132, 383(211), 418(401), 422(401), 428 (401), 435(401), 438(401), 479, 483
- McClement, C. S., 588(548), 611
- McCloskey, C. M., 240(128), 291
- Maccoll, A., 573(504,505), 610
- McConnell, H. M., 20, 21(52), 59, 72, 73, 148(37), 162
- McCoy, R. E., 417(396), 422(396), 483
- McCracken, J. H., 395(281), 480
- McCracken, R., 276(375), 297
- McCreath, N., 222(38), 288
- McDaniel, D. H., 372(152), 376(152), 477
- McDowell, C. A., 63(195), 76, 124(324), 135
- McEwen, K. L., 11-13, 15, 24, 25, 27-29, 31(76), 32, 33, 35(76), 72, 73
- McEwen, W. E., 262(286), 295
- McGlynn, S. P., 120(282), 134
- Machinskaya, I. V., 306(32), 343
- Maciel, G. E., 57, 75
- McIntyre, J. S., 159(74), 163
- McIvor, R. A., 34(115), 35(115), 74
- McKay, A. F., 627(55,56), 632(69), 641(56), 643(102), 644(105), 645(105), 650(110), 655(113,114), 657(114), 660(113), 673 (152,157), 682-684
- McKay, F. C., 491(52), 549(52), 591(52), 592(52), 599
- McKenna, J., 504(306), 605
- MacKenzie, J. C., 629(65,66), 633(66), 634(76), 673(76), 682
- Mackie, R. K., 106(174,175), 119(174,175), 131, 491(215-220), 501(216), 505(216), 506(216), 520(220), 521(215-220), 558 (215,216,218), 560(217), 564(216), 567 (218,220), 571(216), 573(216), 575-577 (216), 603
- McKinney, T. M., 63, 76
- Mackor, A., 203, 204(121,125), 205(121), 211, 212
- McLachlan, A., 55(158), 59(190), 75, 76
- McLean, A. D., 25, 73
- McMahon, R., 188(81), 210
- McMillan, A., 356(64), 373(64), 474
- McMillan, G. R., 220(27), 288
- MacNaughton, N. W., 640(97), 683
- MacNicol, D. D., 159(73), 163
- McRae, E. G., 34(109), 45, 74, 75, 103, 130, 167(7), 209
- McSweeney, J. V., 556, 558(418), 580(418), 608
- McVeigh, P. A., 386(240), 388(240), 389 (240), 479
- McWeeny, R., 532(388), 607
- Madson, E., 106(179), 131
- Maffei, S., 271(346), 297
- Magson, E. H., 411(357), 482
- Mahieu, C., 495(288), 515(288), 516(288), 554(288), 605
- Mahler, G., 228(66,70), 289
- Maimind, V. I., 263(293), 281(411), 295, 298
- Maine, M. M. de, 34(113), 35(113), 74, 91(79), 93, 104(89), 128
- Maine, P. A. D. de, 34(113), 35(113), 69, 74, 77, 91(79,80), 93, 94(80), 104(89), 117(272), 118(272), 120, 128, 133, 134
- Maioli, L., 517(344,345), 564(345), 576 (345), 579(344), 580(344), 606
- Mair, W. S. L., 217(2), 287
- Mairanovskii, S. G., 353(38-42), 354(39, 55), 356(39,42,55), 364(40,42), 365(40), 366(38,39,42,55), 367(139), 372(55), 373 (38-40,55), 472(38), 474, 476
- Mak, S., 402(312), 403(312), 481
- Makarov, S. P., 249(194), 263(194), 267 (194), 269(194), 285(429), 293, 299
- Maki, A. H., 58, 61-63, 76, 122(306), 123, 125(329), 134, 135
- Maksimets, V. P., 90(63), 127
- Maksimovic, M., 103(145), 130
- Malhotra, S. K., 363(95), 475
- Malimonova, A. B., 399(302), 481
- Malinovskii, M. S., 491(232,237), 566(232, 237), 568(232,237), 603
- Malinowski, W., 378(176), 478
- Mallory, F. B., 58(172), 76, 254(230), 265 (307), 294, 296, 461(466), 485
- Mamedova, Y. G., 15(39,40), 72
- Manabe, O., 235(106), 290
- Manatt, S. L., 254(230), 294
- Mandell, H. C., Jr., 617(19), 681
- Manson, D., 242(150), 291

- Maragliano, M. V., 614(13), 628(13), 681  
 Marbet, R., 417(392), 422(392), 445(392),  
 449(392), 450(392), 483  
 Marchetti, G., 233(96), 290  
 Mare, H. E. de la, 217(3), 287  
 Margerum, J. D., 354(77,78), 355(77,78),  
 475  
 Mariella, R. P., 582, 611  
 Marino, G., 582(532), 611  
 Maron, S. H., 353(28-30), 356(29-31,59),  
 364(28), 366(28), 366(59), 368(28), 372  
 (28,59), 373(28,31,59), 375(30), 473(28-  
 31), 474  
 Marshall, H. P., 284(425), 299  
 Marshall, J. H., 124(325), 135  
 Martell, A. E., 274(367), 297  
 Martin, J. S., 56, 57(163), 75, 109(197,  
 198), 131  
 Martinek, M., 272(355), 273(355), 297  
 Martinelli, R., 230(79), 290  
 Martynoff, M., 151(52), 162  
 Martynov, I. V., 324(122), 346  
 Martynova, L. L., 249(194), 263(194), 267  
 (194,322), 269(194), 285(429), 293, 296,  
 299  
 Maruta, S., 103(139,140), 130  
 Maruyama, K., 203(120), 211, 276(378),  
 298  
 Maruyama, Y., 42(133), 43(133), 45(133),  
 75, 95(94), 96(94), 123, 168(13), 209  
 Marvel, C. S., 226(60), 289  
 Masaki, M., 90(78), 128  
 Masar, J. P., 673(151), 684  
 Maschke, A., 266(317), 296  
 Mason, J., 11(22), 13, 14(22), 69, 72, 82  
 (7), 126, 140(16), 145(31), 158(31), 162,  
 202(116), 205(128), 211  
 Mason, S. F., 102(129), 129  
 Massey, E. H., 309(40), 343  
 Matevosyan, R. O., 121(300), 134  
 Matheiu, J. P., 88(48), 90(48), 127  
 Mathur, K. B. L., 564(470), 609  
 Matrel, R. F., 240(137), 291  
 Matsen, F., 172(30), 173(30), 174, 209  
 Matskanova, M. A., 407(342), 482  
 Matsumara, K., 568(480), 610  
 Matsumoto, H., 333(160), 347  
 Matsuoka, O., 45, 75, 96, 128  
 Mattinson, B. J. H., 139(7), 144-146(7),  
 152-154(7), 161, 205(127), 211  
 Maung, M., 564(469), 565(469), 609  
 Mauser, H., 189, 206(133), 210, 212, 246  
 (182), 261(275), 286(182), 292, 295  
 Maxwell, C. E., III, 640(97), 683  
 Mayberry, M. C., 260(252), 294  
 Mayer, H. S., 247(185), 292  
 Mayo, P. de, 166, 181, 186, 208, 210, 212,  
 213  
 Meakins, G. D., 111(219), 132, 302, 303  
 (16), 306(16), 307(16), 323(16,114), 330  
 (16), 343, 345  
 Mecke, R., 114(242), 133  
 Mecklenberg, K. L., 327(138), 346  
 Medhi, K. C., 87, 127  
 Meek, J. S., 425(421a), 438(421a), 445  
 (421a), 451(421a), 484  
 Meen, R. H., 629(62), 631(62), 641(99),  
 655(113), 660(113), 667(129), 673(155),  
 682-684  
 Meer, E. ter, 335, 347, 404, 481  
 Meerssche, M. van, 15(29,30), 72  
 Meinwald, J., 231(84), 290  
 Meinwald, Y. C., 231(84), 290  
 Meis, H., 352(25), 473  
 Meisenheimer, J., 244(161,166,167), 249  
 (192), 292, 293, 352(25), 377(161), 380  
 (199), 416(386), 422(386), 423(386), 473,  
 477, 478, 483, 554(410), 565(474), 608,  
 609  
 Meister, H., 253(217), 260(217), 293  
 Meister, T. G., 153(62), 163  
 Melander, L., 530(386), 531(386), 607  
 Mel'nikov, N. N., 390(266), 391(266), 480  
 Meltzer, R. I., 518(350), 606  
 Meltzer, T. H., 220(28), 271(28), 288  
 Menard, D. F., 260(252), 277(379), 294,  
 298  
 Menzel, H., 460(465), 485  
 Merritt, F. R., 120(292), 134  
 Merritt, W. D., Jr., 491(70), 508-511(70),  
 514(70), 545(70), 547(70), 549(70), 564  
 (70), 571(70), 575(70), 576(70), 599  
 Merrow, R. T., 313(60), 344  
 Mertel, H. E., 581, 582(523), 611  
 Mertens, K. H., 614, 680

- Metzger, H., 208(140), 212, 218(10), 234  
(101), 235(109,110), 236(110), 237(101),  
240(101), 248(109,110), 287, 290, 556  
(417), 608
- Meuche, D., 383(218), 479
- Mevis, M. E. A. H., 228(68), 289
- Meyer, C., 622(35), 681
- Meyer, F., 629(63), 682
- Meyer, J., 340(187), 348
- Meyer, K. H., 353(35,36), 356(36), 373(36),  
406(36), 408(36), 409(35), 416(35), 471,  
474
- Meyer, V., 325, 335, 346, 371(141,142),  
385(141,223), 386(223), 389(243), 390,  
391(142), 394, 396(279), 397, 460(462),  
476, 479-481, 485
- Meyers, E. A., 104(157), 130
- Miarka, S. V., 257(240), 294
- Michalska, M., 314(63), 344, 410(345),  
482
- Michalski, C., 376(179a), 478
- Michel, R., 190(84), 210, 426(427), 484
- Miescher, E., 10(18), 72
- Migdalof, B., 182(67), 210, 354(71), 355  
(71), 475
- Mijs, W. J., 151(46), 162, 253(225), 294
- Milburn, R. M., 471(488), 486
- Milewich, L., 308(39), 309(39), 343
- Miller, A. L., 491(379), 531(379), 607
- Miller, D., 175, 176(40), 209
- Miller, E. W., 364(110), 368(110), 472  
(110), 476
- Miller, F. M., 492(277), 605
- Miller, J., 490-492, 493(120,144,156), 494  
(119,121,153), 495(119,123,125,126,128,  
132,287), 498(123,125,126), 500(151), 507  
(129), 508(120,128,132,139,140,144,150,  
152,160), 509(119,120,123-126,128,132,  
135,136,139-142,144-147,152,157,159),  
510(119,121,123-126,128,129,134-137,  
141-147,320), 511(119-121,123,126,128,  
129,132,136,138,141,144,145,151,152,  
159,160), 512(119,150), 513(150,153,328),  
514, 515(145,149-151,153,159,160), 520,  
533, 534(144,145,152,155), 535(124), 536  
(120,135,139,142,146,147,287), 537(124,  
126,131,141), 540, 541(119,123,132), 542,  
(152,160), 544(121,128,132,136,156), 545  
(156), 546, 548(145), 550, 552(150), 554,  
564(122,139), 566(130,153), 567(153),  
569, 571(159), 576(153,159), 577(153),  
581(154), 598, 601, 605, 606
- Miller, L. J., 354(77), 355(77), 475
- Miller, R. E., 520(362-364), 558(362-364),  
560(362,363), 576(362,364), 607
- Miller, W. R., 232(92), 290
- Milliaresi, E. E., 102(119), 129
- Millikan, A., 302(14), 343
- Mills, C., 278(393), 298
- Minatogawa, H., 576(518), 611
- Minisci, F., 269(330), 296
- Minkin, V. I., 105(169), 131
- Minville, R. M., 240(131), 291
- Mioc, D., 90(60), 127
- Mitchell, M. J., 331(156), 332(156), 347
- Mitchell, S., 207, 208(138), 212
- Miyahara, A., 333(160), 347
- Miyaki, K., 273(357), 297
- Miyazaki, T., 273(357), 297
- Mochalina, E. P., 240(136), 291, 378  
(184a), 478
- Moe, H., 491(54), 510(54), 511(54), 534  
(54), 599
- Moed, H. D., 590(557), 611
- Möller, E., 375(155), 477
- Möller, W., 574(509), 610
- Moffit, W., 21(57), 73
- Mojzis, C., 120(285), 134
- Momigny, J., 181(55), 210
- Monack, L. C., 505(308), 533-535(308),  
605
- Montagne, H. J., 637(88), 682
- Montagne, M., 94, 128
- Montavon, M., 417(392), 422(392), 445  
(392), 449(392), 450(392), 483
- Montmollin, G. de, 555(413), 608
- Montmollin, M. de, 555(413), 608
- Mooberry, D. D., 329(149,150), 330(149,  
150,155), 332(149,150), 334(150), 347
- Mooney, B., 303(18), 343
- Mooney, E. F., 89(57), 127
- Morat, C., 18(49), 20(49), 73
- Morath, R. J., 491(58-60), 495(58,59),  
496(58,60), 497(60), 498(58), 502(58,59),  
503(58-60), 504(60), 540(59), 554(58,60),  
599

- Morgan, G. T., 673(141,142), 684  
 Morgan, K. J., 116(260), 133  
 Moriconi, E. J., 259(244), 294  
 Moritz, A. G., 115, 133  
 Moritz, J., 179(50), 210  
 Morizur, J. P., 109(203), 131  
 Morokuma, K., 24(77), 26(77), 29-31(77), 73  
 Morozova, N. S., 418(400), 453(400), 455(400), 458(400), 459(400), 483  
 Morris, J. W., 111(215), 132, 491(222), 521(222), 558(222), 567(222), 603  
 Morrison, H. A., 165, 182(67), 210, 354(71), 355(71), 475  
 Morton, J. R., 22(62), 73  
 Moscowitz, A., 21(57), 73  
 Moser, C., 7(10), 8, 9(14), 10, 68(14), 71(225), 72, 77  
 Mosher, H., 181(61), 210, 354(67-69,72,77), 355(77), 475, 581(524), 582(535), 611  
 Moss, R. A., 159(72), 163  
 Moumtzis, J., 104(159), 130  
 Moye, A. J., 402(312), 403(312), 481  
 Muceniece, L., 102(131), 130  
 Müller, E., 153(59), 163, 208(140), 212, 218(10), 234(101), 235(109,110), 236(110), 237(101), 240(101), 248(109,110), 287, 290  
 Mueller, N. L., 104(162), 130  
 Mueller, W. A., 100(101), 129  
 Mugnoli, A., 491(192), 567(192), 602  
 Muller, N., 533(390), 607  
 Mulliken, R. S., 10, 24, 72, 73, 116, 133, 520(356), 533(390), 607  
 Mullins, D. D., 223(44), 288  
 Muraour, M. H., 563(465), 609  
 Murov, S., 168(18), 180(53), 209, 210  
 Murphy, A. M., 588(549), 611  
 Murrell, J. N., 14(26), 35(116), 57(168), 66(116), 72, 74, 75  
 Murthy, A. S. N., 113, 132  
 Murto, J., 491, 503(169), 507(162,166-168,173-176), 509(176), 510(169), 511(162), 513(169), 518(174,175), 520(174,175,177-180), 521(172), 529(175), 531(174,175), 533(167,170,173,175), 536(176,180), 542(164), 544(173), 545(175), 546(175), 548(166), 549(162-166,174,176,181), 550(167,173,175), 552(169), 554(162,164-166), 561(162,181), 564(162,172,175,181), 565, 566(162,164,173), 567(172,175,178-180), 568(178-180), 581(177), 602  
 Murto, M. L., 491(173), 507(173), 533(173), 544(173), 550(173), 566(173), 602  
 Murty, T. S. S. R., 112(229), 114(229), 132  
 Musa, M., 102(136), 130  
 Musher, J. I., 55(159), 75  
 Mustafa, A., 271(342), 297  
 Muth, C. W., 333, 347  
 Myers, G. S., 629(66), 633(66), 634(76,78), 645-647(107), 650(110), 655(113), 660(113), 661(121), 667(129), 673(76), 682-684  
 Myers, J. L., 673(139), 674(139), 684  
 Myers, R. J., 32(105), 64(198), 74, 76, 106(181), 124(315), 131, 135, 160, 163
- ## N
- Nadai, G., 570(500), 610  
 Nagakura, S., 11, 13, 14(23-25), 15(23), 34, 35(114,118), 37, 42, 43(133), 45, 64(200), 71(228), 72, 74-77, 92, 95, 96, 105, 106(177), 123(172), 125(177), 128, 131, 148, 149(43), 162, 167(5,11), 168(13), 209  
 Nagarajan, K., 322(110,111), 345  
 Nagata, C., 71(231,232), 77  
 Nagel, W., 103(147), 130  
 Nakadate, M., 560(440), 609  
 Nakamoto, K., 80(4), 81(4), 126, 139(4), 141(19), 142(19), 148(38,39), 161, 162, 202(117,118), 211, 253(223), 293  
 Nakamura, K., 87(39), 127  
 Nakashima, R., 87(39,41-43), 88, 127  
 Namba, K., 84, 90(76), 126, 128  
 Nametkin, S. S., 385(225), 479  
 Nanu, I., 277(384), 298  
 Natterstad, J. J., 57, 75  
 Naukina, M. A., 101(106), 129  
 Neale, A. J., 549(397), 608  
 Neber, P. W., 224(49), 272(351), 289, 297

- Nef, J. U., 313(59), 344, 351, 385(15), 418 (15,404), 422(15,404), 423(15), 444, 445, 446(15), 460(15), 463(473), 464, 473, 484, 485
- Neikam, W. C., 108(196), 131
- Neilands, J. B., 240(132), 260(248), 291, 294
- Neilands, O., 314(67,68), 344, 412(373, 374), 413(373,374), 483
- Neiman, L. A., 263(293), 295
- Neiman, M. B., 15(39-41), 17(41), 72
- Neitzki, R., 245(174), 292
- Nelson, K. W., 509(319), 510(319), 606
- Nenitzescu, C. D., 360(84), 379(84), 381 (84), 382(84), 392(275), 400(84), 401 (84), 402(84,309,313), 404(313), 405(84, 313), 406(84), 417(84,275), 421(275), 422 (275), 448(84), 450(84), 452(84), 462 (275), 463(275), 465(275), 475, 480, 481
- Nenz, A., 229(74), 289
- Nerdel, F., 327(137), 342(137), 346
- Nesbet, R. K., 28(89,91), 73, 74
- Neufer, J. E., 120(286), 134
- Neunhoeffer, O., 276(372), 297
- Nevins, T. E., 363(92), 381(92), 475
- Newall, C. E., 560(441), 609
- Newton, J., 116(260), 133
- Nicholas, D. L., 151(47), 162, 253(224), 293
- Nicholls, M. L., 226(62), 289
- Nicholson, A., 170(24), 209
- Nicholson, D. L., 139(9), 161
- Nickon, A., 321(107), 345
- Nielsen, A. T., 330(154), 335(175), 338 (179), 340(154), 346, 347, 349, 353(50-52), 354(50,51), 356(50,52,58), 357(52), 360(52), 361(52,58), 362(52), 363(103), 366(50,52), 370(50,51), 371(51,52), 372 (51,52), 373(50,52), 380(195), 382(189), 383(52), 385(50,51), 386(51), 391(189), 393(189), 404(323), 431(444a), 473(52), 474, 475, 478, 481, 485
- Nielsen, J. R., 81, 82(5), 89(5), 126
- Nijhoff, D., 200(107), 211, 491(274), 585 (274), 586(274), 605
- Nikitchenko, V. M., 102(135), 130
- Nikolaeva, L. Ya., 153(62), 163
- Nikonova, L. A., 425(423), 455(423), 484
- Nilson, M. E., 314(62), 344
- Nitzer, H., 228(70), 289
- Noble, P., 335(171), 347, 460(460), 485, 491(53), 505(53), 509(53), 510(53), 534 (53), 599
- Noland, T. T., 395(281,283), 404(320), 405(320), 480, 481
- Noland, W. E., 333(162), 339, 347, 348, 350(4), 363(105,106), 385(4), 386(105, 240), 388(240), 389(240), 391(105), 392 (105), 394(105), 473, 476, 479
- Nold, A., 269(334), 296
- Noll, C. I., 650
- Noller, C. R., 260(260), 294
- Nomura, Y., 587(546), 611
- Nordmann, J. B., 329(145), 346, 352(19), 473
- Norman, R. O. C., 68(214,215), 69(214, 215), 76, 238(126), 291, 402(316), 481, 511(323), 520(323), 550(323), 551(323), 606
- Norris, A. D., 364(119), 476
- Norris, R. K., 144(23), 151(23), 160(23), 162
- Norris, W. P., 245(171), 292
- Norrish, R. G. W., 170(23), 209, 219(20), 285(432), 288, 299
- Norwitz, G., 90(68), 128
- Novikov, S. S., 84(22), 89(54), 94(90), 126-128, 340, 348, 353(38-40,42,43), 354(39,55), 356(39,42,55), 364(40,42), 365(40), 366(38,39,42,55,115,117), 367 (139), 371(153), 372(55), 373(38-40,55, 115,117,145,146,148), 374(115,117,145, 146,148,150,151,156), 375(153,156), 378 (178,181,182), 380(146,178), 383(150, 178,206), 395(181,182,285,286), 396(181, 286), 397(288,289), 418(398,400,402), 436 (423), 431-433(436), 435(402,449), 436 (178), 453(398,400,436,456-458), 454 (398,456), 455(398,400,423,456), 456(398, 456,458), 457(456-458), 458(398,400,436, 456,457,458a), 459(400,457), 460(461, 464), 472(38), 474, 476-478, 480, 481, 483-485
- Noyes, R. M., 674(163), 684
- Nudenberg, W., 220(28), 271(28), 288
- Nukada, K., 231(85), 290

Nussim, M., 168(18), 180(53), 209, 210  
 Nygaard, E. M., 395(281-283), 396(282),  
 404(320), 405(320), 480, 481  
 Nysted, L. N., 308(38), 343

**O**

Oac, S., 281(410), 298  
 Ochai, E., 582(536), 611  
 O'Connor, P. R., 341(192), 348  
 Oddo, B., 290  
 Oehlert, H., 195(95), 211  
 Oesterling, R. E., 89(56), 90(56), 127  
 Offenbacher, M., 15(33), 72  
 Offermann, K., 277(386), 298  
 Ofstead, R., 176(43), 209  
 Ogata, Y., 229(73), 271(347), 279(394),  
 281(394), 289, 297, 298, 568, 569(477),  
 610  
 Ogg, R. A., Jr., 674(164), 684  
 Ogloblin, K. A., 230(82), 231(86), 264  
 (297), 290, 295  
 Ogushi, T., 235(106), 290  
 Ohashi, M., 577(519), 611  
 Ohno, M., 231(85), 264(296), 290, 295  
 Oishi, K., 261(266), 295  
 Okafor, E. C., 491(27), 512-514(27), 531  
 (27), 598  
 Okamoto, M., 231(85), 290  
 Okamoto, T., 491(59,63-65), 495(59), 502  
 (59), 503(59), 540(59), 589(64), 599  
 Okamura, I., 241(141), 291  
 Okano, M., 568, 569(477), 610  
 Okawara, R., 274(368), 297  
 Okhlobystina, L. V., 373(145), 374(145),  
 477  
 Okon, K., 468(479), 469(479), 486  
 Oksengendler, G. M., 491(235), 560(235),  
 568(235), 603  
 Okuda, M., 125(336), 135  
 Okuyama, T., 577(519), 611  
 Olah, G. A., 111(217), 132  
 Olah, J. A., 111(217), 132  
 Oleinikova, K. N., 120(288), 134  
 Olguin, J., 104, 130  
 Oliveto, E. P., 329(147,149,150), 330(149,  
 150), 332(149,150), 334(150), 346, 347  
 Olsson, A., 111(222), 132

Olviero, A., 568(476), 610  
 Onishchenko, A. A., 458(458a), 485  
 Opolski, S., 421(413), 422(413), 484  
 Oppelt, J. C., 247(186), 292  
 Oppenheimer, R., 3, 71  
 Orchin, M., 91(84), 92(84), 128  
 Orgel, L. E., 147(36), 162, 202(115), 211  
 Orlova, E. Yu., 564(471-473), 571(471,  
 472), 609  
 Orndorff, W. R., 226(62), 289  
 Orpwood, G. W. F., 564(469), 565(469),  
 609  
 Orton, K. J. P., 620, 681  
 Ostromisslenski, I., 244(160), 292  
 Ostrovskaya, S. V., 491(257), 505(257),  
 551(257), 604  
 O'Sullivan, D. G., 83(13), 126, 140, 162  
 Otha, M., 90(78), 128  
 Ott, W. L., 627(55), 682  
 Ottens, R., 417(395), 419(395), 422(395),  
 483  
 Ouellette, R. J., 363(102), 475  
 Overchuk, N. A., 111(217), 132  
 Owston, P. G., 623(41), 628(59), 681

**P**

Pabst, P., 232(90), 286(435), 290, 299  
 Pace, R. J., 145(30), 146(30), 162  
 Pagano, A. S., 306, 307(30,34), 343,  
 378(184), 395(184), 418(401), 422(401),  
 428(401), 435(401), 478, 483  
 Pai, B. R., 322(110,111), 345  
 Pain, D. L., 250(201), 293  
 Palenik, G. J., 23(66), 73  
 Palinchak, S., 385(205), 402(205), 452(205),  
 478  
 Palmer, K. J., 11(19), 72  
 Palmer, M. H., 255(231), 256(231), 294  
 Pan, C. Y., 81(5), 82(5), 89(5), 126  
 Panckhurst, M. H., 368(125), 476  
 Papanastassiou, Z. B., 304(25), 306(25),  
 343  
 Parcell, L., 205(129), 212, 266(318), 296  
 Parham, W. E., 341(192), 348, 388(239),  
 479  
 Paris, J., 191(87), 211

- Pariser, R., 7(6), 42(6), 71
- Park, J. D., 218(13), 222(38), 231(88),  
287, 288, 290
- Parker, A. J., 491, 492(146), 500(151),  
508(150), 509(145,146), 510(134,137,  
145,146), 511(100,145,151), 512(101,150),  
513(150), 514(100), 515(145,149-151),  
518(99), 520(98,100), 534(145), 536(146),  
540(101,134,137,145,146,149-151),  
546(98), 548(98,145), 550(97,98),  
552(100,150), 553(100), 554(101),  
557(97,101,421), 600, 601, 608
- Parker, C. O., 111(227), 132, 326(132),  
346, 418(401), 422(401), 423(418),  
428(401,418), 429(418), 435(401),  
438(401), 483, 484
- Parker, R. E., 491(79,80,85), 492(279,  
282), 495(85), 496(85), 497(79), 500(85),  
501(79,80,279,295), 502(80,85), 504(79,  
279), 505(79,80,85,279,295), 506(79,85,  
279,295), 518(79), 520(79), 523(382),  
524(382), 529(79,382), 532, 540(295),  
541(295), 542(85), 544(85), 545(79,279,  
295), 546(79,295,382), 551(79), 552(79),  
562(279,295), 564(279,295), 565(295),  
578, 579(282), 580(282), 581, 600, 605,  
607
- Parks, L. R., 501(294), 504-506(294),  
517(346), 520(294,346), 541(294),  
545(294), 550(346), 551(346), 552(294),  
605, 606
- Parr, R. G., 7(6), 42(6), 71
- Passailaigue, P., 354(67), 475
- Passerini, M., 263, 287(436), 295, 299
- Passing, H., 271(343), 297
- Pastor, R. C., 121(294), 134
- Paszyc, S., 172(28), 175, 209
- Patai, S., 102(122), 129, 515(333), 606
- Patchett, A. A., 37(120), 74, 305, 307(28),  
343
- Patinkin, S. H., 673(153), 684
- Patterson, J. A., 302(3), 342
- Patterson, J. M., 321(106), 345
- Patterson, L. J., 88(48), 90(48), 127,  
145(28), 162, 671(136), 684
- Patterson, T. S., 356(64), 373(64), 474
- Pattison, F. L. M., 327(135), 346
- Patton, J. T., 329(144,145), 346,  
352(18,19), 473
- Patzig, E., 244(166), 249(192), 292, 293,  
554(410), 608
- Paul, M. A., 284(426,427), 299
- Pauling, L., 5(3), 32(103), 71(229),  
71, 74, 77
- Pavlovskaya, I. V., 249(194), 263(194),  
267(194), 269(194), 293
- Peacock, D. H., 550(398), 608
- Peacock, T. E., 96(98), 128
- Pearson, B. D., 103, 130
- Pearson, R. G., 356(56,57), 364(57,112),  
365(57,112), 366(56), 367(57,112, 138),  
372(57), 373(56), 374(56), 376(56),  
407(341), 461(112), 473(112), 474, 476,  
482, 552(403), 608
- Pechet, M. M., 221(34), 222(35), 288
- Pechmann, H. v., 269(334), 296, 595,  
596(569), 612
- Pechmann, V., 620(28), 638(28), 640(28),  
681
- Pedersen, K. J., 365, 370(133), 476
- Pel'kis P. S., 102(125), 129
- Perekalin, V. V., 84(27), 90(73), 116(262),  
126, 128, 133, 328(141), 333(141), 346,  
362(89-91), 390(264), 475, 480
- Perham, W. E., 596(579-581), 612
- Perkins, M. J., 490(13), 529(13), 598
- Perrit, G., 558(432), 608
- Perrotti, E., 220(24), 288
- Person, J. T., 243(157), 292
- Person, W. B., 116(266), 133, 520(356),  
607
- Peschke, W., 103(147), 130
- Pesrin, V. G., 579(522), 611
- Peterson, C. J., 102(126), 111(226), 129,  
132
- Peterson, R. C., 491(105,108,109,111),  
497(111), 503(105,108,109,111),  
524(105,108,109,111), 525(105,108,109,  
111), 530(105,108), 531(108), 566(108),  
600
- Petit, R., 109(203), 131
- Petrov, A. A., 111(214), 132
- Petruska, J., 50, 75
- Pettijean, C., 279(395), 298

- Peuré, F., 561(454,455), 564(454,455),  
 568(454), 609  
 Pfeiffer, P., 197(98), 211  
 Pfeilsticker, K., 360(86), 380(86),  
 415(86), 475  
 Pfister, K., 327(138), 346  
 Pfeiderer, W., 226(58), 289, 582(529–  
 531), 611  
 Philippe, R. J., 139(8), 161  
 Phillips, J. P., 102, 130  
 Phillips, L., 266(317), 296  
 Phillips, L. V., 219(16), 288  
 Phillips, W. D., 155(67), 156(67), 163  
 Picard, J. P., 461(468), 485, 673(152,155),  
 684  
 Piccinini, C., 174(34,36), 209  
 Pickard, R. H., 273(359), 297  
 Pickett, L. W., 533(390), 607  
 Pier, S. M., 333(159), 347  
 Pierce, O. R., 386(233), 388(233), 479  
 Pieroni, A., 280(407), 298  
 Pierson, E. H., 302(5), 342  
 Pietra, F., 491, 500(91,95), 501(91,93,  
 94,96), 504(91,93,94,96), 522(91,96),  
 523(93), 525(91,93,94,96), 526(92), 529  
 (92), 530(91,92), 531(92), 533(94),  
 541(94,95), 542(94,95), 545(94), 571(92),  
 600  
 Pietrandrea, J., 120(285), 134  
 Piette, L. H., 37(121), 38(121), 62(121),  
 74, 121(302), 134  
 Pilcher, G., 26(88), 73  
 Piloty, O., 235, 240(129), 260(108),  
 286(129), 290, 291, 391–393(274), 480  
 Pimental, G., 172(27), 209  
 Pinchas, S., 84, 86(37), 89, 90(37), 115,  
 126, 133  
 Pinguair, A., 513(332), 531(332),  
 539(332), 606  
 Pinhey, J., 178(47), 210  
 Pink, P., 426(426,428), 427(426), 484  
 Pinnow, J., 261(264), 294  
 Pino, P., 102(133), 130  
 Piotrowska, H., 90(66), 127  
 Piret, P., 15(29), 72  
 Pisecky, J., 558(431), 608  
 Pisha, T. A., 270(337), 296  
 Piskorz, M., 146(32), 153(32), 162  
 Piskunova, Zh. P., 491(240), 568(240),  
 571(240), 603  
 Pistor, G., 261(264), 294  
 Pitsaris, V. K., 244(164), 292  
 Pitts, J., Jr., 166, 167(2), 170(1,2), 172(33),  
 173(33), 174(38), 186(38), 208(141),  
 208, 209, 212, 213, 584(543), 611  
 Pitzer, C. L., 411(348), 482  
 Pivawer, P. M., 107(188), 116, 131,  
 311(56), 312(56), 344, 406–410(330),  
 482  
 Placek, L., 86(32), 126  
 Plapinger, R. E., 390(251), 479  
 Platt, E. N., 380(195), 478  
 Plazek, E., 582(533), 611  
 Plummer, C. W., 325–327(124), 346  
 Pockels, U., 315(74), 344  
 Podgornova, V. A., 230(78), 289  
 Podleshka, P., 675(166), 684  
 Poizat, L., 264(301), 295  
 Polansky, O. E., 596(582), 612  
 Pollitt, R. J., 520(367), 532(389), 557(423),  
 558(389,423), 559, 560(389), 561(389),  
 566(367), 607, 608  
 Ponomareva, E. A., 102(123), 129  
 Pople, J. A., 7(7), 28(89), 54(154), 55,  
 71, 73, 75  
 Popov, E. M., 84, 126  
 Porai-Koshits, B. A., 223(47), 224(50),  
 283, 289  
 Poroshina, L. I., 113(232), 132  
 Porter, P. K., 226(60), 289  
 Porto, A. M., 491(49), 498(49), 502(49),  
 514(49), 534(49), 535(49), 537(49),  
 540(49), 550(49), 599  
 Potasznik, D., 502(297), 504(297),  
 534(297), 535(297), 605  
 Powell, H. M., 119(277), 134  
 Powers, J. W., 330–333(151), 334(170),  
 347, 366(116), 373(116), 374(116),  
 376(116), 476  
 Preibisch, R., 390(255,256), 391(255,256),  
 480  
 Prelog, V., 328(139,140), 346  
 Preobrazhenskii, N. A., 410(343,344),  
 421(344), 424(344), 448(344), 482  
 Price, C. C., 318(90), 345, 414(378), 483  
 Price, W. C., 31(97), 74



Priebs, B., 176(42), 209  
 Prijs, B., 621(32), 622(32), 642(32), 681  
 Pring, J. N., 284(424), 299  
 Priou, R., 179(49), 210  
 Pristera, F., 84, 126  
 Pritchard, H. O., 26(87), 73, 219(21), 288  
 Pritchett, W. A., 386(232), 388(232),  
 398(232), 479  
 Pritzkow, W., 228(66,70), 231(87),  
 232(90), 256(237), 286(435), 289, 290,  
 294, 299  
 Privezenteva, N. F., 285(429), 299  
 Prokhoda, A. M., 491(237), 566(237),  
 568(237), 603  
 Prokhorova, N. I., 503(300-302), 533  
 (300,301), 536(302), 605  
 Prosser, J. H., 511(323), 520(323),  
 550(323), 551(323), 606  
 Protopopova, N. P., 113(232), 132  
 Pruitt, K. M., 491(67, 68), 501(67),  
 503(67,68), 504(68), 505(67), 506(67,68),  
 520(67), 525-527(68), 530(68), 531(67),  
 542(67), 545(67), 549(67), 554(68),  
 564(67), 571(67,68), 572(67), 573(67),  
 576(67,68), 599  
 Pryde, E. H., 232(92), 290  
 Pulford, A. G., 144(25), 145(25), 162  
 Pummerer, R., 275(370), 297  
 Pupko, L. S., 102(125), 129  
 Purlee, E. L., 284(425), 299  
 Pusch, E., 406(332), 411(332), 482

## Q

Quaife, M. L., 152(57), 163  
 Quilico, A., 269(330), 296  
 Quinn, M. J., 542(395), 578-580(395),  
 599, 608

## R

Raasch, M. S., 319(97), 345  
 Radmic, S., 103(145), 130  
 Ragle, J. L., 58(180), 62, 63(180), 76  
 Raikova, T. P., 236(117), 291  
 Raimondi, M., 491(193), 532(193), 602  
 Rajagopalan, P., 459(459), 485  
 Rall, K. B., 111(214), 132  
 Ramachrandran, L. K., 104(163), 130

Ramakrishnan, V., 505(309), 520(365),  
 558(309,365), 571(365), 575(365),  
 577(365), 605, 607  
 Ramart-Lucas, P., 151(52), 162  
 Ramasseul, R., 15(36), 17-19(36), 72  
 Ramsay, O., 200(109), 201(109), 211,  
 583(539), 584(539), 586(539), 611  
 Randall, E. W., 57(167), 65(204), 75, 76  
 Randall, J. J., 491(72), 501(72), 504(72),  
 506(72), 520(72), 523(72), 524(72),  
 528(72), 530(72), 541(72), 545(72), 600  
 Randle, R. A., 85, 126  
 Rao, B. D. N., 109(200), 131  
 Rao, C. N. R., 34(112), 74, 79, 80(2),  
 82(2), 83, 86, 88(52), 89(2,52), 90(52),  
 91(85), 92(85), 93, 94(87), 95(85),  
 96(85), 100, 101(85), 102(85), 103, 113,  
 114, 120, 125-130, 132, 134, 137, 138(3),  
 139(3), 142(3), 147-149(35), 161, 162,  
 383(216), 479  
 Rapchinskaya, S. E., 491(233), 566(233),  
 568(233), 603  
 Rascanu, R., 274(362), 297  
 Rassat, A., 15(36,42), 16(42), 17(36,42,44),  
 18(36,42,46,49), 19(36,42,44), 20(48-50),  
 21(42,44,48,50,56,61), 22(48), 68(48),  
 69(48), 70(42), 72, 73, 261(273), 295,  
 304(23), 343  
 Rastrup-Andersen, J., 23(71), 32(71), 73  
 Rathbone, P., 220(26), 288  
 Ratovskii, G. V., 102(112), 129  
 Ratz, F., 400(306), 418(403), 419(403),  
 422(306,403), 438(403), 443(403), 481,  
 483  
 Rauhut, M. M., 491(56,62), 530(56),  
 592(62,562), 599, 612  
 Rauscher, H., 224(49), 272(351), 289,  
 297  
 Ravet, J. P., 261(273), 295  
 Ray, F. E., 382(205), 402(205), 452(205),  
 478  
 Ray, J. D., 58(171), 75, 674(164), 684  
 Razuvayev, G. A., 15(38), 72  
 Read, T. O., 492(279), 501(279,295),  
 504(279), 505(279,295), 506(279,295),  
 532(295), 540(295), 541(295), 545(279,  
 295), 546(295), 562(279,295), 564(279,  
 295), 565(295), 605

- Reagan, H., 101(102a), 129  
Reasoner, J., 176(44), 177(44), 209,  
388(235), 389(235), 479  
Reasoner, W., 179-181(48), 210  
Rebbert, R., 170, 172(25), 175(25), 210  
Reed, W. L., 335(171), 347, 460(460), 485  
Rees, C., 201(112), 211, 490, 491(84),  
529(11,13), 582(84), 587(545), 598,  
600, 611  
Reich, W. S., 419(410), 422(410),  
423(410), 428(410), 484  
Reid, C., 120(279,281,289), 134  
Reid, S., 186, 210, 212  
Reihlen, H., 273(361), 297  
Reilly, E. L., 155(67), 156(67), 163,  
219(17), 288  
Reilly, J., 568(482), 610  
Reinders, W., 562(459), 609  
Reinert, K. E., 106(183), 311  
Reinhard, R., 206(130), 212  
Reinheimer, J. D., 491(73), 500(73),  
501(73,292), 503(292), 505(292), 506  
(292), 507-509(73), 510(321), 514(73),  
524(321), 530(387), 545(292), 549(73),  
550(73), 579(520), 580(520), 582(387),  
600, 605-607, 611  
Reinhold, D., 327(138), 346  
Reinisch, R. F., 262(281), 275(281), 295  
Reinmuth, W. H., 58(182), 76  
Reissert, A., 469(484), 486  
Reitz, D. C., 21(54), 73  
Reitz, O., 367(134), 476  
Rennev, G., 251(208), 293  
Rérat, C., 23(68), 73  
Reverdin, F., 562(461), 609  
Rey, P., 18(49), 20(49), 73  
Reynolds, W. F., 109(199), 131  
Rheinboldt, H., 235, 238(113), 290,  
469(480), 486  
Ribaldone, G., 229(74), 289  
Ricca, A., 391(274a), 392(274a),  
469(274a), 480  
Ricci, A., 581(525), 611  
Ricciello, S. R., 240(137), 291  
Rice, D. E., 222(36,39), 288  
Rice, F. O., 329(146), 346  
Richards, J. H., 55(158), 75  
Richards, R. E., 58(169), 75, 110(208),  
132  
Richmond, H. H., 632(69), 655(114),  
657(114), 661(121), 682, 683  
Richter, H. J., 582(538), 611  
Richter, V. v., 591, 592(559,560), 612  
Richtmyer, N. K., 434(443), 485  
Rickett, R. M. W., 424(420), 447(420),  
448(420), 484  
Ridd, J. H., 557(425), 558(425), 575(515),  
608, 610  
Ridgewell, B. J., 88(46b), 127  
Riebel, A. H., 243(156), 264(304), 292,  
296  
Ried, W., 199(101), 207(136), 211, 212  
Riegel, E. R., 673(145), 684  
Rieger, P. H., 58(182,183), 59-61,  
62(187,193), 76, 124(327), 135  
Rigaudy, J., 90(77), 128  
Rigby, G. W., 319(97), 345  
Riley, E. F., 350(2), 473  
Riley, J. P., 103(142), 130  
Rilliet, A., 325(123), 335, 346, 460(462),  
485  
Rinckenberger, A., 373(147), 460(147),  
477  
Ringer, W. E., 562(458,459), 609  
Ringold, H. J., 324(120,121),  
333(120,167), 346, 347, 363(93,94),  
475  
Rinks, I. J., 245(169), 292  
Rising, A., 240(134,138), 271(349),  
272(349), 283(349), 291, 297  
Rist, M., 555(414), 608  
Ritchie, C. D., 365(121), 367(121), 476  
Rivoire, G., 125(340), 135  
Rizzardo, E., 178(47), 210  
Roberts, E., 224(49), 289, 656(115), 683  
Roberts, E. M., 113(237), 132  
Roberts, J. D., 57, 58(166), 175,  
110(209,210), 111(210), 132, 331(157),  
347  
Roberts, K. C., 589(551), 611  
Robertson, P. W., 271(350), 297  
Robertson, W., 411(356), 482  
Robins, J. M., 101, 129  
Robinson, C. H., 308(39), 309(39), 343  
Robinson, E. B., 276(371), 297

- Robinson, L., 112(229), 114(229), 132  
 Robinson, R., 555(412), 608  
 Robson, E., 235(107), 266(313), 274(313),  
 290, 296  
 Robson, J. H., 633(70), 682  
 Rochester, C. H., 104(160), 130,  
 201(111), 211, 491(195-203), 520(197),  
 521(195-203), 526(384), 558(195,197,  
 200,201), 566(202,484,485),  
 567(196,199,200,202), 568(483-485),  
 575(197-199,203,384,483), 587, 602,  
 607, 610  
 Rodano, G. A., 250(199), 293  
 Rodig, O. R., 591(558), 612  
 Rodionov, V. M., 306(32), 343  
 Rodowskas, E. L., 329(146), 346  
 Roesler, W., 228(70), 289  
 Rogers, N., 207(139), 212, 259(245), 294  
 Rogle, J. L., 124(322a), 135  
 Rogowski, F., 11(20), 72  
 Rohde, G., 260(256), 294  
 Rohleder, J., 113(234), 132  
 Rohrbaugh, P. E., 501(292), 503(292),  
 505(292), 506(292), 545(292), 605  
 Rolewicz, H. A., 90(62), 111(227), 127,  
 132, 418(401), 422(401), 428(401),  
 435(401), 438(401), 483  
 Rollefson, G., 172(27), 209  
 Romburgh, P., 574 (511,512), 610, 614,  
 628(57,58), 633(72), 637(82), 680-682  
 Roney, B. D., 116(263), 133  
 Roos, E., 272(353), 297  
 Roothaan, C. C. J., 6(5), 28(5,90), 34(5),  
 71, 74  
 Rosanoff, N., 383(214), 479  
 Rose, G. G., 94(91), 128, 167(10), 209,  
 419(410), 422(410), 423(410), 428(410),  
 484  
 Rose, J. D., 248(191), 292, 417-420(394),  
 422-424(394), 438(394), 442(394), 443,  
 446(394), 451(394), 452(394), 459(394),  
 483  
 Roseeu, A., 276(374), 297  
 Roselaar, L., 170(22), 209  
 Rosenberg, R. M., 253(220), 293  
 Rosenblum, M., 247(183), 292, 593, 594,  
 612  
 Rosenfelder, W. J., 323(119), 346  
 Rosenthal, J., 23(71), 32(71,102), 73, 74  
 Rosenthal, R., 378(179a), 478  
 Roser, C., 273(356), 297  
 Ross, S. D., 490, 491, 496(110), 497,  
 501(102), 502(110), 503(103-111),  
 504(103,104), 505(107), 506(107),  
 524(102-111), 525(102-111), 526(107),  
 530(105,107,108), 531, 545(107),  
 553(110), 566(108), 600, 649, 650, 660  
 Rossi, S., 330(153), 332(153), 347  
 Rostaing, P., 362(87), 475  
 Rothenberg, R. V., 261(265), 294  
 Roux-Guerraz, C., 220(23), 288  
 Rowlands, J. R., 22(62), 73  
 Rozantzev, E. G., 15(39-41), 17(41), 72  
 Rozhkov, I. N., 374(149), 477  
 Rubaszewska, W. T., 104(154), 130  
 Ruccia, M., 250(220), 293  
 Rudloff, P., 228(70), 289  
 Rüegg, R., 417(392), 422(392), 445(392),  
 449(392), 450(392), 483  
 Ruehlmann, E., 228(66), 289  
 Ruetschi, W., 661, 683  
 Ruff, F., 229(75), 289  
 Ruff, I., 240(129), 286(129), 291  
 Ruggli, P., 254(228), 279(395,397),  
 294, 298  
 Rundle, R. E., 141(19), 142(19), 153(59),  
 162, 163, 202(118), 211, 253(223), 293  
 Ruse, M., 260(261), 261(261), 294  
 Ruske, E., 276(372), 297  
 Russell, E. R. R., 255(231), 256(231), 294  
 Russell, G. A., 58(176), 76, 190(85),  
 191, 192, 210, 211, 262(284), 276(377),  
 282(284), 295, 298, 395(280), 398(280),  
 399(305), 402(305,312,314,315), 403  
 (312,315), 422(314), 426(314,428a),  
 428(314,428a), 480, 481, 484, 558(427),  
 608  
 Russell-Hill, D. Q., 491(88), 600  
 Rüst, E., 389(244), 479  
 Rustad, N. E., 582(538), 611  
 Ruyle, W. V., 327(138), 346  
 Ruzicka, E., 272(355), 273(355), 297  
 Ryason, P. R., 491(53), 505(53), 509(53),  
 510(53), 534(53), 599  
 Ryhage, R., 425(422), 461(422), 484

Ryser, G., 417(392), 422(392), 445(392),  
449(392), 450(392), 483

Ryzhmanov, Y. M., 121(300), 134

## S

Saari, W. S., 426(428b), 428(428b), 484  
Sachs, F., 185, 186(74,77), 210, 246(179),  
277, 292, 298

Sadler, P. W., 83(13), 126, 140, 162

Safonova, E. N., 353(43), 474

Sah, P. P. T., 640(98), 673(156), 675,  
683, 684

Sahhar, F., 262(281), 275(281), 295

Saito, E., 354(77), 355(77), 475

Saito, T., 273(357), 297

Sakaguchi, T., 560(448), 609

Sakai, I., 264(296), 295

Sakurai, R., 241(141), 291

Salkowski, H., 569(486,487), 610

Salomaa, P., 385(227), 479

Samartsev, M. A., 231(86), 264(297),  
290, 295

Sammy, G., 573(504), 610

Samokhvalov, G. I., 410(343,344),  
421(344), 424(344), 448(344), 482

Samosvat, L. S., 271(345), 282(415), 297,  
298

Samuel, D., 86(37), 89(37), 90(37), 126,  
592, 612

Sánchez, M. B., 324(120), 333(120), 346,  
363(93), 475

Sand, H., 272(352), 297

Sandel, V., 200(103), 211

Sander, A., 353(35), 409(35), 416(35),  
474

Sandorfy, C., 115(253), 133, 673(157),  
684

Sane, K. V., 121(298,299), 134

Sarbhay, K. P., 564(470), 609

Sargent, F. B., 123(313), 135, 191, 211

Sastry, L. V. S., 104(163), 130

Satake, K., 577(519), 611

Sato, R., 261(276), 295

Sato, Y., 151(49), 162

Saucy, G., 417(392), 422(392), 445(392),  
449(392), 450(392), 483

Sauer, J., 490, 598

Sauers, C., 181(61), 210

Saunders, B. C., 520(367), 532(389),  
557(423), 558(389,423), 560(389), 561,  
566(367), 607, 608

Saunders, D. R., 388(242), 479

Saunders, R., 181(56), 182(69), 210

Saunders, S. L. M., 569(490), 610

Savell, W. L., 470(486), 486

Savides, C., 88-90(52), 127, 311(51,54),  
344, 383(216), 411(363), 479, 482

Savige, W. E., 576(517), 610

Savolainen, M., 552(407), 608

Savory, J., 218(14), 287

Savost'yanova, I. A., 431-433(436),  
453(436), 458(436), 484

Savrov, S. D., 125(338), 135

Sbarbati, N. E., 491(47,48), 496(47),  
498, 502(47,48), 524(47), 530(47),  
534(48), 537(48), 552(47), 599

Scaife, C. W., 319(92-96), 345, 390(267),  
391(267), 480

Schaal, R., 561, 564(454,455), 566(454),  
609

Schaefer, H., 232(90), 256(237), 286(435),  
290, 294, 299

Schaefer, T., 107(186), 109(199), 111(212),  
131, 132

Schäffner, S., 225(55), 289

Scharf, M., 661(119), 683

Schaub, R. E., 111(221), 132, 312(57),  
313(57), 344, 406(334), 407(334),  
409(334), 410(334), 482

Schechter, H., 388(230), 398(230), 479

Scheinbaum, M., 194, 211

Schellman, J. A., 21(58), 73

Schenk, G. H., 120(285), 134

Schickh, O. v., 400(307), 481

Schiessler, 649, 650, 660

Schiff, R., 381(202), 478

Schindler, R., 139(19), 151(51), 162

Schippa, G., 230(79), 290

Schlatzer, R. K., 591(558), 612

Schleyer, P. v. R., 112, 114, 132

Schmidpeter, A., 146(34), 162

Schmidt, C. H., 277(385), 298

Schmidt, F. H., 103(147), 130

Schmidt, J., 232(93), 250(199), 290, 293,  
597(586), 612

- Schmidt, O., 397(296,297), 398(296,297), 400(296), 401(296), 419(297), 424(296, 297), 481
- Schmitz, E., 352(21), 453(21), 473
- Schmitz, R., 363(104), 475, 559, 560 (435,436), 608, 609
- Schneider, W. G., 54(154), 56(161), 75, 111(212), 132
- Schoenbrunn, E. F., 230(78), 289, 319(95), 345
- Schofield, K., 383(217), 479
- Scholl, R., 623(43), 645, 646, 649, 681
- Schonberg, A., 268(328), 271(328), 278(328), 296
- Schors, A., 257(239), 294
- Schreck, J. O., 86(33), 101(104), 126, 129
- Schrier, B., 530(387), 582(387), 607
- Schroeder, W. A., 673(154), 684
- Schroetler, H. W., 125(343), 135
- Schubert, W. M., 101, 129
- Schueller, K. E., 265(307), 296, 461(466), 485
- Schug, J. C., 59, 76
- Schultz, G., 260(256), 294
- Schultze, O. W., 350(1), 351(1), 353(33), 362(1), 377(1), 380(1,33), 381(33), 399(33), 460(1), 471(1,33), 472(1), 473, 474
- Schulz, K., 260(251), 294
- Schuster, P., 596(582), 612
- Schwam, H., 37(120), 74, 305(28), 307(28), 343
- Schwartz, J. R., 253(222), 293
- Schwartz, M., 633(71), 682
- Scigliano, J. J., 335(174), 336(174), 347
- Scoggins, L. E., 101(105), 129
- Scoggins, M. W., 103(141), 130
- Scott, C. B., 552(399), 608
- Scott, E. W., 471(489), 486
- Scott, G. R., 504(305), 550(305), 551(305), 605
- Scott, L. B., 667(128), 683
- Scurti, F., 237(121), 290
- Sears, C. A., 318(90), 345
- Seelert, K., 556(417), 608
- Seidel, P., 418(405,406), 422(405,406), 446(405,406), 484
- Seidl, V., 240(133), 270(133), 291
- Seigle, L. W., 302(4), 342, 405(328), 428(328), 482
- Seiler, M. K., 125(337), 135
- Sekiya, M., 261(266), 295
- Seligman, R., 241(144), 242(144), 291, 359(83), 378(83,180), 380(83,180), 395(83,180), 475, 478
- Semenov, L. V., 353(43), 474
- Semper, L., 394(277), 397(277), 480
- Sen, A. B., 570(498), 610
- Serafin, B., 90(66), 127
- Serebryany, S. B., 102(123), 129
- Serre, J., 24(82,83), 73
- Servis, K. L., 377(169), 477, 521(375,376), 531(375,376), 567(375), 575(375), 607
- Servoz-Gavin, P., 18(46), 72
- Severin, T., 363(104), 380(191), 383(213), 414(191,213,382), 415(213), 418(191), 419(191), 420(191,213), 421(213), 422(191), 423(191), 424(213), 436(213), 437(213), 444(213), 447(191,213), 475, 478, 479, 483, 559, 560(435-437), 608, 609
- Seyerwetz, A., 264(301), 295
- Shakhova, M. K., 410(343, 344), 421(344), 424(344), 448(344), 482
- Shamma, M., 207(135), 212, 261(274), 295
- Shanley, E. S., 308(35), 343
- Shapiro, B. L., 249(193), 268(324), 293, 296
- Shapiro, B. S., 266(317), 296
- Sharp, J., 172(33), 173(33), 209
- Sharter, J. J., 491(90), 533(90), 550(90), 551(90), 600
- Shatenstein, A. I., 558(428), 559, 608
- Shavel, J., 518(350), 606
- Shaver, F. W., 333(159), 347
- Shchekotikhin, A. I., 249(194), 263(194), 267(194), 269(194), 293
- Shechter, H., 84(25), 105(167), 126, 131, 302, 319, 336-339, 341(189), 343, 345, 347, 348, 350(10), 362(10), 383(210), 402(311), 414(381), 418(408), 422(408), 426(425), 427(425), 432(408), 436(408), 473, 478, 483, 484
- Shedlovsky, T., 356(31), 373(31), 473(31), 474

- Sheehan, J. C., 660(118), 683  
 Shelegova, O., 172(29), 209  
 Shemyakin, M. M., 263(293), 281(411),  
 295, 298  
 Sheperd, R. G., 490, 581, 582(16), 598  
 Shepherd, J. W., 84(25), 126, 311(51),  
 344, 350(10), 362(10), 473  
 Sherman, E., 674(153), 684  
 Sherred, J. A., 411(362), 482  
 Shevelev, S. A., 89(54), 94(90), 127, 128,  
 340(184), 348, 366(117), 371(153),  
 373(117,146,148), 374(117,146,148,150,  
 156), 375(153,156), 380(146), 383(150,  
 206), 397(288,289), 418(402), 426(423c),  
 435(402), 460(464), 463(469), 467(469),  
 468(469), 476-478, 480, 481, 483-485  
 Shilor, E. A., 576(516), 610  
 Shimanskaya, M. V., 103(143), 130  
 Shimobayashi, Y., 576(518), 611  
 Shimura, H., 152(56), 163  
 Shindo, H., 249(196), 293  
 Shingu, H., 71(231), 77  
 Shinoda, T., 577(519), 611  
 Shlyapochnikov, V. A., 84, 126, 383(206),  
 478  
 Shman'ko, I. I., 114(240), 115(250), 132,  
 133  
 Shoolery, J. N., 111(223), 132  
 Short, L. N., 139(9), 161  
 Shpanskii, V. A., 249(194), 263(194),  
 267(194), 269(194), 293  
 Shriner, R. L., 328(142), 346, 352(17),  
 381(204), 400(204), 402(310), 405(310),  
 406(327), 420(411), 421(204), 422(411),  
 423(417), 429(327,411,417), 443(411),  
 445(417), 447(204), 448(411), 450(417),  
 452(411), 462(411), 463(411), 466(411),  
 473, 478, 481, 484  
 Shrivastava, R. D., 232(91), 290  
 Shutov, G. M., 564(471-473), 571(471,  
 472), 609  
 Sidgwick, N. V., 253(218), 256(218),  
 258(218), 265(306), 284(423), 293, 296,  
 299  
 Sidman, J., 66(210), 76  
 Silber, P., 183, 186(75), 210, 246(176),  
 278(388), 292, 298  
 Silberg, A., 272(355), 273(355), 297  
 Silver, B. L., 86(37), 89(37), 90(37), 126  
 Simanska, M., 103(143), 130  
 Simmons, H. E., 331(157), 347  
 Simmons, P., 88(46a), 127  
 Simmons, T., 88, 127, 389(247), 390(247),  
 406-408(333), 479, 482  
 Simonetta, M., 491, 492(186,187),  
 493(190), 494(182,186,188,189),  
 503-506(190), 507(184), 510(190),  
 511(190), 520(190), 532, 533(185),  
 567(192), 578(186), 579(182-190), 580,  
 581(189), 602, 386(241), 388(241),  
 405(324), 479, 481  
 Simpson, D. M., 31(97), 74  
 Singh, A., 550(398), 608  
 Singh, K., 84(16), 126  
 Singh, S., 113, 114, 132  
 Sinonov, A. M., 105(169), 131  
 Sioda, R., 105, 128, 263(287), 295  
 Sitz, H., 352(22), 389(22), 473  
 Sixma, F. L. J., 504(307), 533(307),  
 541(307), 550(307), 605  
 Sjöberg, B., 155(65), 163  
 Skarre, O. K., 491(239), 566(239),  
 568(239), 603  
 Skinner, H. A., 26(87, 88), 73  
 Skolnik, S., 625(52), 682  
 Skoropisova, T. S., 491(257), 505(257),  
 551(257), 604  
 Skulski, L., 115(246), 116(261), 133  
 Slagg, N., 172, 175(25), 209  
 Slettinger, M., 327(138), 346  
 Sloan, G. J., 21(53), 73  
 Slovetskii, V. I., 89(54), 94(90), 127, 128,  
 366(115,117), 371(153), 373(115,117,  
 145,146,148), 374(115,117,145,146,148,  
 150,151,156), 375(153,156), 380(146),  
 383(150,206), 418(402), 435(402,449),  
 460(461,464), 476-478, 483, 485  
 Slovokhotova, N. A., 116(262), 133  
 Smagin, S. S., 453(455-457), 454(456),  
 455(456), 456(456,458), 457(456,458),  
 458(457,458), 485  
 Smart, G. N. R., 617(21), 629(66),  
 633(66), 634(76,77), 647(21), 673(76),  
 681, 682  
 Smentowski, F. J., 160(76), 163,  
 262(283), 295

- Smeykal, K., 228(66,70), 289  
 Smidt, J., 595(575), 612  
 Smiles, S., 588, 590(553-555), 611  
 Smiley, R. A., 35(117), 74, 82(6), 83(6),  
 90(6), 92(86), 126, 128, 325(126,130),  
 326(126), 327(136), 346, 386(232),  
 388(232), 398(232), 429(434), 479, 484  
 Smirnov, L. V., 104(155), 130  
 Smirnov, V. V., 395(284), 396(284), 480  
 Smith, D. C., 81(5), 82(5), 89(5), 126  
 Smith, D. M., 557(424), 558(424),  
 564(424), 608  
 Smith, G. B. L., 624(47), 625(52), 682  
 Smith, G. W., 340(186), 341(188), 348  
 Smith, H. E., 309(40), 343  
 Smith, L. I., 234(103), 290, 341(193),  
 348, 430(444), 485  
 Smith, M. A., 102(111), 129  
 Smith, P. A. S., 217(1), 236(114), 248(188),  
 252(215), 254(215), 261(277), 266(314),  
 269(333), 280(405), 287, 291-293, 295,  
 296, 298, 350(3), 473  
 Smith, R. H., 213, 379(188), 478  
 Smolinsky, G., 379(187), 478  
 Smoyer, R. B., 520(359), 607  
 Smyth, C. P., 15(32), 42(131), 48(131), 72,  
 75, 116(258), 133  
 Snatzke, G., 167(9), 209  
 Sneed, M. C., 391(271), 480  
 Snipes, R. F., 491(61), 495(61), 514(61),  
 534(61), 599  
 Soanes, P. W., 491(80,85), 495(85), 496  
 (85), 500(85), 501(80), 502(80,85), 505  
 (80,85), 506(85), 542(85), 544(85), 600  
 Sobotka, W., 84(24), 126  
 Sof'ina, E. N., 223(47), 288  
 Sogulyaeva, V. M., 102(123), 129  
 Sokolov, S. D., 435(448), 485  
 Sokovishina, I. F., 328(141), 333(141), 346  
 Soldate, A. M., 674(163), 684  
 Solomonovici, A., 90(74), 128  
 Solonina, B., 272(355), 273(355), 297  
 Solvet'skii, V. I., 84(22), 126  
 Somasekhara, S., 200(103), 211, 583(541),  
 611  
 Sopova, S., 390(264), 480  
 Souchay, P., 353(45,46,48,49), 385(46),  
 386(46), 400(48), 474  
 Souers, C., 354(69), 475  
 Sourissau, G., 90(58), 127  
 Sousa, J., 125(339), 135, 191(88), 211, 354  
 (66,74,75,80), 355(66,75,82), 383(74,75),  
 475  
 Sowden, J. C., 385(220), 479  
 Spanagel, E. W., 341(194), 348  
 Spanberger, L. R., 125(346), 135  
 Spano, F. A., 259(244), 294  
 Speakman, J. C., 623(41), 681  
 Specht, P., 352(22), 389(22), 473  
 Spedding, B. G., 139(15), 141, 142(15),  
 143(15), 162  
 Spencer, T., 364(108), 476  
 Spengeman, W. F., 629(64), 682  
 Spielmeyer, G., 469(482), 486  
 Spiesecke, H., 56(161), 75  
 Spinner, E., 105(166), 131  
 Spittler, G., 182(68), 210  
 Splitter, J., 195, 198, 211, 465(477), 470  
 (477), 486  
 Sprenkels, E., 574(514), 610  
 Springall, H. D., 667(127), 683  
 Sprung, M. M., 244(163), 260(163), 292  
 Sribnaya, V. B., 491(237), 566(237), 568  
 (237), 603  
 Stamm, R., 470(487), 486  
 Stanevich, A. E., 113, 115(235), 132  
 Stanko, H., 87(38), 126  
 Stanko, V. I., 90(75), 128  
 Stansfield, F., 491(155), 514(155), 534  
 (155), 540(155), 601  
 Stanton, D. W., 111(216), 132  
 Starcher, P. S., 107(187), 131, 316-319  
 (83), 345, 409(337a), 482  
 Starr, L. D., 582(535a), 611  
 Stashkov, L. I., 121(300), 134  
 Staudinger, H., 267(321), 296  
 Stavorski, J., 327(138), 346  
 Steadly, H., 101(109), 129  
 Steele, V., 315(69), 344, 411(359), 482  
 Stefani, A. P., 218(13), 231(88), 287, 290  
 Stefaniak, L., 38(122), 74, 106(184), 107  
 (185), 110(207), 114(245), 131-133, 363  
 (97), 475  
 Steff, E. P., 462(470), 463(470), 466(470),  
 485  
 Steger, A., 561(449,450), 609

- Steigmann, A., 272(355), 273(355), 297  
 Stein, G. A., 327(138), 346  
 Stein, R. A., 582(534), 611  
 Steinbock, H., 391–393(274), 480  
 Steinhoff, G. W., 268(327), 296  
 Steinkopf, W., 316(80), 318(89), 344, 345, 378(176), 380(176), 389(249,250), 391(249), 392(249,250), 393(250), 395(249), 407(249), 418(407,409), 422(407), 423(407), 435(409), 438(407,409), 445(409), 465(249), 478, 479, 484  
 Stephenson, C. V., 70(222), 77  
 Sterescu, M., 102(136), 130  
 Stern, E. S., 102, 130  
 Sternhell, S., 144(23), 151(23), 160(23), 162  
 Stetter, H., 340(187), 348, 431(446), 485  
 Stevens, T. E., 266(318), 296, 320(99), 333(163), 340(183), 345, 347, 348  
 Stevenson, P. E., 50, 75  
 Stiegelman, A., 282(413), 298  
 Stille, J. K., 332(164), 333(164), 347  
 Stizman, M. E., 374(148a), 477  
 Stock, A., 235(108), 260(108), 290  
 Stockel, R. F., 247(186), 292  
 Stoermer, R., 195(95), 211, 411(346), 482  
 Stone, C. A., 327(138), 346  
 Stone, E. W., 63, 76  
 Stone, J. F., Jr., 354(65), 362(65), 378(65), 386(65), 389(65), 398–401(65), 417(65), 422(65), 435(65), 474  
 Stoner, G. A., 262(281), 275(281), 295  
 Storch, L., 251(206), 293  
 Stothers, J. B., 110(205), 132  
 Stradins, J., 125(334), 135, 412(373,374), 413(373,374), 483  
 Strahm, R. D., 404(319), 405(319), 481  
 Strausz, O. P., 219(19), 288  
 Streitwieser, A., Jr., 7(9), 55(9), 56, 71(224), 71, 77  
 Strom, E., 204(123), 211, 212, 276(377), 298, 339(305), 402(305), 481, 558(427), 608  
 Strumza, J., 90(74), 111(228), 128, 132  
 Stryker, H. I., 261(267), 295  
 Stuart, F., 240(128), 291  
 Stuart, R. S., 640(96), 683  
 Stuckey, R. E., 684  
 Stüber, O., 325, 335(123), 346  
 Suarez, T. H., 491(47), 496(47), 498(47), 502(47), 524(47), 530(47), 552(47), 599  
 Sugahara, H., 322(108), 345, 370(140), 476  
 Suggitt, J. W., 629(66), 633(66), 645–647(107), 682, 683  
 Suhr, H., 38(123), 74, 491, 499(113,116–118), 500(112–114,116–118), 501(118), 502(113,114), 503(113), 505(114), 506(113,114), 515(334), 522(115), 524(115), 526(115), 527(115), 529(115,116), 533(113), 541, 543(114), 544(114), 548(114), 550(113), 552(116–118), 554(115), 561(114), 564(114), 571(114), 573(114), 576(114), 600, 601  
 Sukhomlinov, A. K., 90(63), 127  
 Sultanov, A., 90(65), 127, 244(164), 292  
 Sunagawa, G., 151(49), 162  
 Sunamoto, J., 212  
 Sundararajan, V. N., 322(110,111), 345  
 Sundberg, R. J., 213  
 Sunde, E., 260(258), 294  
 Supan, A., 378(176), 380(176), 478  
 Suprunenko, A. I., 104(155), 130  
 Suschitzky, H., 379(188), 478  
 Sutcliffe, H., 222(40), 288  
 Sutcliffe, L. H., 213  
 Suter, C. M., 561(453), 609  
 Sutton, L. E., 65(202,204), 77  
 Sutulei, Y., 90(71), 128  
 Suzuki, K., 148(38), 162, 202(117), 211  
 Suzuki, Y., 90(72), 103(139,140), 128, 130  
 Svastal, S., 271(341), 297  
 Svátek, E., 145(29), 162  
 Swain, C. G., 552(399,400), 608  
 Swern, D., 310(44), 343  
 Swift, A. H., 335(174), 336(174), 347  
 Symons, E. A., 556(419), 558(419), 608  
 Symons, M. C. R., 32(100), 74, 121(301), 123(301,309,310), 124, 134, 135  
 Syrovatka, I. G., 491(257), 505(257), 551(257), 604  
 Szeki, T., 259(243), 294  
 Szolayksi, B., 260(257), 271(348), 272(348), 294, 297

T

- Tabei, K., 148(43), 149(43), 162  
 Taboury, F. J., 90(60), 127



- Taft, R. W., 59, 63(184), 76, 534(405), 551(405), 608
- Takabayashi, F., 101(107), 129
- Takagi, Y., 271(347), 279(394), 281(394), 297, 298
- Takayama, H., 332(164), 333(164), 347
- Takeuchi, T., 90(71,72), 103(140), 128, 130
- Talaty, C. N., 459(459), 485
- Talaty, E. R., 402(312), 403(312), 481
- Talik, T., 226(59), 265(59), 289, 514(330), 606
- Talik, Z., 226(59), 265(59), 289, 503(299), 505(299), 507(299), 510(299), 511(299), 514(330), 582, 605, 606, 611
- Taller, R. A., 156, 157(69), 163
- Talvik, A., 376(158), 477
- Tamelen, E. E. van, 304(23), 343
- Tanabe, K., 111(220), 132, 323(113), 345
- Tanabe, T., 241(141), 291
- Tanaka, I., 23(69), 66(209), 73, 76
- Tanaka, J., 11(23), 13, 14(23), 15(23), 32, 42(132), 72, 74, 75, 96(97), 128, 148(42), 162, 266(315), 296
- Tanaka, M., 11(23), 13, 14(23), 15(23), 72, 148(42), 162
- Tanaka, T., 274(368), 297
- Tanasescu, I., 181(59), 186, 197(97), 210, 211, 260(261), 261(261), 277(384), 294, 298, 379(186), 478
- Tanikaga, R., 203(120), 211
- Tannenbaum, E., 32(105), 74, 106, 131
- Tannenbaum Handelsman, E., 32(106), 74
- Tannenwald, P. F., 125(342), 135
- Tarr, A. M., 219(19), 288
- Tarrant, P., 218(14), 287
- Tartakovskii, V. A., 84(22), 94(90), 126, 128, 373(146), 374(146), 380(146), 383(206), 418(398,400), 425(423), 431-433(436), 435(449), 543, 454(398,456), 455(398,400,423,456), 456(398,456,458), 457(456-458), 458(398,400,436,456,457,458a), 459(400,457), 460(461), 477, 478, 483-485
- Tarte, P., 139, 144(14,26), 146(5,14), 147(14), 161, 162
- Tatlow, J. C., 496(285), 497(285), 500(285), 508(285,318), 554(318), 605, 606
- Taturi, A. D. M. D., 102(133), 130
- Taub, B., 325(125), 326(125), 327(125), 136), 346
- Taurins, A., 671(138), 684
- Taverne, H. J., 637(87), 639(87), 682
- Taylor, F. L., 234(103), 290
- Taylor, G. W., 627(55), 682
- Taylor, H. J., 428(430), 484
- Taylor, R. C., 501(292), 503(292), 505(292), 506(292), 545(292), 605
- Taylor, W. J., 105(167), 131, 383(210), 478
- Tedder, J. M., 235(107), 266(313), 274(313), 290, 296
- Teeter, H. M., 232(92), 290
- Teijin Ltd., 220(29), 288
- Temme, H. L., 559(436,437), 560(436, 437), 609
- Tench, A. J., 124(323), 135, 246(181), 292
- Tereshkevich, M. O., 491(239), 566(239), 568(239), 603
- Terpugova, A. F., 115(254), 133
- Testa, A. C., 48(145), 75, 174(37), 183(73), 209, 210, 212, 213
- Tetel'baum, B. I., 267(322), 296
- Tewari, K. S., 151(54), 163
- Tewfik, R., 102(115), 129
- Thackaberry, S., 179-181(48), 210
- Thakur, R. S., 453(453), 485
- Thang, K. V., 90(77), 128
- Theilacker, W., 161(78), 163, 204(124), 211, 252(213), 293, 333(161), 347, 352(20), 473
- Theobald, R. S., 383(217), 479
- Thiede, R. J., 248(190), 292, 385(221), 386(221), 388(221), 479
- Thiele, J., 411(347), 482, 614, 616, 622, 623(39), 624, 625, 681, 682
- Thoma, M., 560(438), 609
- Thomas, A. T., 667(127), 683
- Thomas, J. R., 15(35), 17-79(35), 21(60), 68(35,216), 72, 73, 76, 172(31), 209
- Thomas, S. S., 218(4), 220(27), 287, 288
- Thomas, W. J. O., 89, 90, 127
- Thompson, A. R., 151(48), 152(55), 162, 163
- Thompson, C. C., Jr., 117(272), 118(272), 133

- Thompson, H. W., 139, 141(18), 142(18), 161, 162
- Thompson, T. J., 491(225), 521(225), 560(225), 561(225), 603
- Thomson, R. H., 115(252), 133
- Thorn, G. D., 673(149), 684
- Thurston, J. T., 381(204), 400(204), 420(411), 421(204), 422(411), 429(411), 443(411), 447(204), 448(411), 452(411), 462(411), 463(411), 466(411), 478, 484
- Timmons, R. B., 122(305), 134, 172(26), 209
- Titarenko, N. I., 491(259), 505(259), 604
- Titov, A. I., 264(305), 296, 351(75), 344, 395(284), 396(284), 480
- Todd, A., 453(455), 485
- Todd, Lord, 453(453), 485
- Todesco, P. E., 581(525), 611
- Toggweiler, U., 262(280), 295
- Tolles, W. M., 32(106), 74
- Tomilenko, E. J., 576(516), 610
- Tommila, E., 491(164,181), 542(164), 549(164,181), 552(407), 554(164), 561(181), 564(181), 566(164), 602, 608
- Tonkyn, R. G., 491(53), 505(53), 509(53), 510(53), 534(53), 599
- Tonolo, A., 251(211), 293
- Toombs, L. E., 629(67), 682
- Topham, A., 182(69), 210
- Toranzo, R. L., 491(50,51), 497(50), 502(50,51), 524(50,51), 529(51), 530(50,51), 531(50,51), 553(50), 599
- Torchiana, M. L., 327(138), 346
- Toren, P. E., 125(332), 135
- Torrey, H. A., 278(389), 298
- Torrey, J., Jr., 414(377), 483
- Torsell, K., 418(339), 425(399,422,423a, 423b), 433(423b), 461(422), 483, 484
- Touster, O., 234(100), 256(234), 290, 294
- Towne, E. B., 620(30), 621(30), 638(30), 681
- Townes, C. H., 120(293), 134
- Townley, E. R., 221(31,33), 222(31,33), 253(219), 288, 293
- Townsend, J., 59(188), 76
- Tozer, B. T., 590(554), 611
- Trager, W. F., 38(124), 74, 107(189), 131, 363(98,99), 475
- Traynelis, V. J., 556, 558(418), 580(418), 608
- Traynham, J. G., 158(71), 163
- Treon, J. F., 471(489), 486
- Trivich, D., 120(286), 134
- Trofil'kina, V. P., 399(302), 481
- Trotman, J., 14(27), 72, 139(15), 141, 142(15), 143(15), 149(44), 150(44), 162, 252(214), 255(214), 293
- Trotman-Dickinson, A. F., 674(159), 684
- Trotter, J., 40(128), 75
- Troutman, H. D., 307, 314(33), 343
- Truce, W. E., 588(549), 611
- Trueblood, K. N., 673(154), 684
- Trumbore, C. N., 266(319), 296
- Trunov-Krasovski, V. I., 491(234), 511(234), 568(234), 603
- Truter, M. R., 23(72), 73
- Tsai, T. T., 262(286), 295
- Tschirner, F., 241(139,140), 291
- Tschitschibabin, A. E., 354(79), 475
- Tsekhanskii, R. S., 102(127), 129
- Tsenter, M. Y., 125(344), 135
- Tsitsishvili, G. V., 115(251), 133
- Tsoukalas, S. N., 243(158), 292
- Tsubomura, H., 64(200), 76, 105(172), 123(172), 131
- Tsuchida, M., 271(347), 297
- Tsukerman, S.V., 102(135), 130
- Tukevich, B. M., 153(60), 163
- Tundo, A., 517(338-343), 564(340), 577(343), 606
- Tung, C. C., 223(46), 288
- Turitsyna, N. F., 574(508), 610
- Turkevich, J., 120(293), 134
- Turnbull, D., 356(59), 366(59), 372(59), 373(59), 474
- Turner, E. E., 569, 610
- Turner, W. B., 320(100), 345, 390(265), 480
- Turnowska-Rubaszewska, W., 383(207, 208), 478
- Turro, N., 167(4), 209
- Turyan, Ya. L., 364(109), 368(128), 373(109,128), 476
- Tyurin, Yu. M., 368(128), 373(128), 476

## U

- Ue-eda, R., 274(368), 297  
 Uehleke, H., 251(209), 293  
 Ueno, K., 280(409), 281(409), 298  
 Uffmann, H., 161(78), 163, 204(124),  
 211, 252(213), 293  
 Ugi, I., 277(386), 298  
 Uhlfelder, E., 624(48,49), 682  
 Ulbricht, T. L. V., 414(378), 483  
 Ullman, E. F., 594, 612  
 Ullmann, F., 570(499,500), 610  
 Ulmann, R. M., 151(46), 162, 253(225),  
 294  
 Ulpiani, C., 250(199), 293  
 Umbgrove, H., 638(92), 683  
 Umezawa, B., 249(196), 293  
 Una, S. J., 491(28,31), 509(28), 534(28),  
 535(28), 598, 599  
 Ungnade, H. E., 35(117), 74, 82(6), 83(6),  
 90(6), 92(86), 102(132,134), 112-114,  
 126, 128, 130, 132, 237(120), 291, 315  
 (73), 325(125), 326(125,134), 327(125,  
 134,136), 329(134), 339(181), 344, 346,  
 348, 569, 610  
 Urbánski, T., 38(122), 74, 84(21,24), 88  
 (51), 90(66,67), 106(184), 107(185), 110  
 (207), 114, 115, 126, 127, 131-133, 146  
 (32), 153(32), 162, 363(97), 389(245),  
 390(268,269), 391(268,269), 463(471),  
 464(245), 475, 479, 480, 485, 562(456,  
 457), 563(466,467), 609, 667(127), 683  
 Urbschat, E., 240(127), 291  
 Urry, G. W., 426(424), 427(424), 484  
 Uschold, R., 365(121), 367(121), 476  
 Ustravshchikov, B. F., 230(78), 289  
 Ustynyuk, L. A., 463(469), 467(469), 468  
 (469), 485  
 Utley, J. H.P., 103, 130  
 Uzan, A. T., 280(408), 298  
 Uzin, A. T., 286(434), 299

## V

- Vaichunaite, B. K., 281(411), 298  
 Vainionpaa, J., 491(179), 520(179), 567  
 (179), 568(179), 602  
 Vainshtein, F. M., 576(516), 610  
 Vanags, E., 314(65,66), 344

- Vanags, G., 314(65,67), 344, 408(336), 412  
 (336,365-371,373,374,376), 413(336,365-  
 371,373,374,376), 414(380), 460(366), 461  
 (366), 482, 483  
 Vance, P. W., 120(285), 134  
 Vandenbelt, J. M., 50, 75  
 Vanderbilt, B. M., 302(1,2), 342  
 Van der Heyden, A., 200(108), 211, 212  
 Van Dolah, R. W., 313(60), 344  
 Vane, F. M., 108(193), 131  
 Vanino, L., 273(360), 297  
 Van Kalvaren, W., 264(300), 295  
 Van Meersche, M., 252(216), 293  
 Van Raalte, M. A., 356(62), 380(62), 464,  
 474  
 Van Tamelen, E. E., 248(190), 292, 385  
 (221), 386(221), 388(221), 479  
 Van Vleck, J. H., 8(12), 72  
 Varsanyi, G., 91(83), 128  
 Vasilenko, Z. I., 90(70), 128  
 Vasil'eva, L. N., 558(428), 608  
 Vasil'eva, V. N., 116(262), 133  
 Vaughan, J., 504(305), 550(305), 551(305),  
 605  
 Vaughan, W. E., 217(3), 287  
 Vaughan, W. R., 21(53), 73, 144(22), 162,  
 363(96), 475  
 Vecchiotti, L., 174, 184(35), 209  
 Veillard, A., 20-22(48), 68(48), 69(48), 73  
 Veinberg, A. Ya., 410(343), 482  
 Veit, A., 353(32), 354(32), 356(32), 358  
 (32), 365-367(32), 374(32), 380(32), 386  
 (32), 398(32), 404(32), 405(32), 407(32),  
 460(32), 468, 474  
 Velzen, J. C. van, 595(570-574), 612  
 Vember, T., 180(54), 210  
 Venkataraghaven, R., 83, 86, 100(100),  
 126, 129  
 Venkateswarlu, P., 109(200), 131  
 Venker, H. P., 596(583), 612  
 Venter, K. K., 102(124), 129  
 Verkade, P. E., 59, 76, 223(44), 233(98),  
 288, 290, 493(281), 505(281), 534(404),  
 539(281), 541(281), 551(404), 605, 608  
 Vero-Barcellona, L., 251(211), 293  
 Vessel, E. D., 332(164), 333(164), 347  
 Vestling, M. M., 363(92a), 365(92a), 637-  
 370(92a), 475

Vil'davskaya, A. I., 111(214), 132  
 Ville, J., 318(88), 345  
 Vincent, B. F., 311(55), 344  
 Vischer, E., 328(139), 346  
 Vitala, A., 491(180), 520(180), 536(180),  
 567(180), 568(180), 602  
 Vitali, D., 491(96), 501(96), 504(96), 522  
 (96), 525(96), 600  
 Vitenberg, I. G., 579(522), 611  
 Vivarelli, P., 581(525), 611  
 Vlaar, H. T., 557(420), 558(420), 608  
 Vogel, A. J., 675(168), 678(168), 684  
 Vogt, I., 197(99), 211  
 Voigt, K., 383(212), 411(361), 479, 482  
 Voisey, M. A., 218(7), 219(18), 265(310),  
 287, 288, 296  
 Vompe, A. F., 574(508), 610  
 Voorst, J. van, 203, 204(121), 205(121),  
 211, 212  
 Vorländer, D., 574(514), 610  
 Vries, S. de, 491(271), 584(271), 586(271),  
 605  
 Vroom, A. H., 657(116), 683  
 Vuk, N., 242(152), 291  
 Vylegzhonina, N. N., 124(321), 135

**W**

Wacker, L., 282(412), 298  
 Wada, M., 274(368), 297  
 Waddington, T. A., 274(363), 297  
 Wadman, S. K., 590(556), 611  
 Wagnière, G., 1, 21(59), 40(129,130), 41  
 (130), 42(129), 43(130), 44(129), 46(129,  
 130), 48(129), 51-53(129), 65(201), 66  
 (201), 73, 75, 76  
 Wahren, M., 256(237), 294  
 Wajer, T., 203, 204(121), 205(121), 211,  
 212  
 Wakerman, N., 226(60), 289  
 Waldmüller, M., 310(49), 344, 360(85),  
 381(85), 471(85), 475  
 Walker, A. J., 435(447), 485  
 Walker, L. A., 223(44,46), 288  
 Wallace, R., 159(73), 163  
 Walser, A., 328(140), 346  
 Walsh, A. D., 23(73), 25, 73, 144(25),  
 145(25), 162

Walter, H., 226(58), 289  
 Walter, J., 5(4), 6(4), 71  
 Walter, R. I., 121(298), 134  
 Wan, J., 166(1), 170(1), 208  
 Wanags, G., 314(64), 344  
 Wang, S. S., 520(359), 607  
 Wang-Chiang, Ma., 113(233), 132  
 Ward, E. R., 561(452), 609  
 Ward, R. L., 58(173-175), 76, 122(307),  
 123, 124(316), 134, 135, 181(63), 210  
 Warner, P. L., Jr., 207(135), 212, 261  
 (274), 295  
 Warren, K. S., 316(81), 344  
 Wasif, S., 102(115), 129  
 Wat, E. K. W., 315(71), 344  
 Watanabe, H., 65, 76  
 Watanabe, K., 31(96), 74  
 Watarai, S., 87(41,42), 88(41), 127  
 Watatani, M., 151(49), 162  
 Waters, J. H., 326(131,132), 346, 423(418),  
 428(418), 429(418), 484  
 Waters, W. A., 240(130), 291  
 Way, J. W., 219(17), 288  
 Weaver, W. M., 329(148), 330(148), 333  
 (166), 334(148,166,170), 346, 347  
 Webster, B. M., 223(44), 288  
 Webster, M. S., 284(428), 299  
 Weibezahn, K., 380(199), 478  
 Weidner, H., 321(107), 345  
 Weil, J. A., 109(204), 121(298,299), 132,  
 134  
 Weinstein, B., 385(228), 479  
 Weinstein, J., 175(41), 176(41), 191, 199,  
 209, 211, 212, 354(66,74,75,80), 355(66,  
 75,82), 383(74,75), 475  
 Weisblat, D. I., 315(72), 344  
 Weise, J., 399(304), 481  
 Weisler, L., 417(387), 422(387), 426(387),  
 427(387), 429(387), 445(387), 450(387),  
 483  
 Weiss, M. J., 111(221), 132, 312(57), 313  
 (57), 344, 406(334), 407(334), 409(334),  
 410(334), 482, 623(40), 681  
 Weissbach, O., 516, 606  
 Weissman, S. I., 21(54), 59(188), 73, 76,  
 123(308a), 134  
 Weitz, E., 411(347), 482  
 Wells, C. F., 106(176), 131

- Wells, P. R., 109(201,202), 131  
 Welz, H., 399(304), 481  
 Wendel, K., 331(156), 332(156), 347  
 Wendtland, G., 333(161), 347, 352(20), 473  
 Wensink, I. W., 574(512), 610  
 Wepster, B. M., 59, 76, 493(281), 505 (281), 534(404), 539(281), 541(281), 551 (404), 605, 608  
 Werner, E. G. G., 233(98), 290  
 Wertheimer, P., 353(36), 356(36), 373(36), 406(36), 408(36), 471(36), 474  
 West, W., 34(111), 74  
 Westland, L., 675(166), 684  
 Wettermark, G., 125(339), 135, 182, 210, 354(76), 355(76,81), 475  
 Weyerstahl, P., 230(80), 232(89), 290, 322(109), 345  
 Wheland, G. W., 39(127), 71(229,230), 74, 77, 356(60), 366(60), 373(60), 474  
 Whiffen, D. H., 22(62), 70, 73, 77, 85, 126, 139(15), 141, 142(15), 143(15), 162  
 Whitaker, A. C., 319(97), 345  
 White, A. M., 327(136), 346  
 White, E. H., 88(50), 111(50), 127, 145 (27), 162, 238(124), 291  
 White, J. C. B., 105(166), 131  
 White, J. E., 564(469), 565(469), 609  
 White, R. C., 205(129), 212, 266(318), 296  
 White, R. W., 327(135), 346  
 White, S. M., 304(25), 306(25), 343  
 White, W. N., 614(16), 616(16), 681  
 Whitesell, J. K., 207(135), 212, 261(274), 295  
 Whitmore, F. C., 334(169), 347, 650  
 Whitmore, F. E., 618(25), 681  
 Whitmore, M. G., 334(169), 347  
 Wiberley, S. E., 80(3), 82(3), 126  
 Wichterle, O., 240(133), 270(133), 271 (341), 291, 297  
 Wick, G., 47, 75  
 Wiehler, G., 433(439), 485  
 Wieland, H., 15(33), 72, 261(267), 276, 295, 297, 310, 320(102), 321, 344, 345, 394(277), 397(277), 406(329), 407(329), 411(329), 412(329), 429(433), 462(433), 465(478), 480, 482, 484, 486  
 Wieland, T. H., 303(20), 343  
 Wiesenfeld, A. W., 151(47), 162, 253(224), 293  
 Wilcox, P. E., 673(154), 684  
 Wilcox, W. S., 70(222), 77  
 Wild, U. P., 38(126), 39(126), 74, 167 (12), 209  
 Wilder-Smith, A. E., 319(93,95), 345, 390 (267), 391(267), 480  
 Wildman, R. B., 388(236), 479  
 Wildman, W. C., 369(129), 370(129), 385 (226), 388(226,236,242), 395(226), 400 (226), 476, 479  
 Wilk, M., 199(101), 207(136), 211, 212  
 Wilkinson, P. A., 323(114), 345  
 Wilkinson, P. T., 96(98), 128  
 Will, G. M., 271(350), 297  
 Will, W., 397(287), 480  
 Willenz, J., 224(51), 289  
 Willgerodt, C., 246(175), 292, 568(481), 610  
 Williams, A., 181(56), 182(69), 210  
 Williams, A. L., 661(123), 683  
 Williams, D., 181(57), 210  
 Williams, F. T., Jr., 105(167), 131, 383 (210), 388(230), 398(230), 478, 479  
 Williams, F. V., 367(138), 476  
 Williams, H. D., 340(186), 348  
 Williams, R. B., 32(99), 74  
 Williams, R. L., 83, 126, 145, 146(30), 162  
 Williams, V. A., 491(123,125,132,136,141, 287), 492(125), 495(123,125,132,287), 498(123,125), 508(132), 509(123,125,132, 136,141), 510(123,125,136,141), 511(123, 132,136,141), 536(287), 537(141), 540 (123,125,132,136,141), 541(123,132), 544 (132,136), 546(132), 601, 605  
 Williams, W., 182(70), 210  
 Willig, F., 103(147), 130  
 Willis, C. J., 218(8), 265(311), 266(320), 287, 296  
 Willstätter, R., 378(177), 380(177), 381 (177), 460(177), 478  
 Wilms, H., 272(353), 297  
 Wilshire, J. F. K., 501(296), 605  
 Wilson, E. B., Jr., 5(3), 71, 106, 131, 252(212), 293  
 Wilson, I. R., 153(58), 163  
 Wilson, R., 123(313), 135

- Wilson, W., 419(410), 422(410), 423(410), 428(410), 484
- Windaus, A., 323(117,119), 346
- Winkler, C. A., 493(280), 513(280), 514 (280), 605, 657(116), 661, 683
- Winstein, S., 386(241), 388(241), 479
- Winters, L. J., 614(15), 616(15), 628(15), 681
- Wippel, H. G., 277(382), 298
- Wislicenus, W., 310, 344, 360(85,86), 380 (86,193,196,197,200), 381(85,200), 403 (193,196,197), 404(193,196,317), 415(86), 417(196), 420(93,196), 422(193,196), 444 (197), 471(85), 475, 478
- Witanowski, M., 38(122), 74, 106(184), 107(185), 110(207), 114(245), 131-133, 363(97), 475
- Wittek, H., 670, 671, 684
- Wittig, G., 315(74), 344
- Wohl, A., 244(168), 292, 555(415), 608
- Wolf, H., 37(119), 74, 167(8), 209
- Wolfarth, E. F., 614(16), 616(16), 681
- Wolff, L., 303(17), 343
- Wolfram, 670
- Wong, K. W., 491(156,157,160), 493(156), 508(160), 509(157,160), 511(160), 514 (156,160), 515(160), 520(156,160), 533 (160), 540(156,157,160), 542(160), 544 (156), 545(156), 546, 550(156,160), 601
- Wood, C. S., 254(230), 265(307), 294, 296, 461(466), 485
- Woodcock, D., 628(59), 682
- Woodward, R. B., 21(57), 73, 228(71), 289
- Worden, E. F., 266(318), 296
- Worms, C. G. M. de, 589(551), 611
- Wormser, H. C., 325(129), 346
- Worstall, R. A., 390(263), 480
- Wren, H., 380(200), 381(200), 478
- Wright, C. M., 337, 347
- Wright, G. F., 146(33), 160(33b), 162, 613, 617(21), 618(26), 620(26,30), 621 (30), 622(33), 625(51), 629(62,65-67), 631(62), 632(69), 633(66,70,72), 634(76-78), 638(30), 640(96), 641(99), 643(103), 644(104-106), 645(103,105-107), 646 (107), 647(21, 107), 650(110), 655(113, 114), 657(114), 660(113), 661(121), 667 (129), 670(130), 671(137), 673(76,139), 674, 675(139,165,166), 676(137,162,169), 678(170,171), 681-684
- Wu, T. K., 54(155), 55, 56, 75
- Wubbels, G., 202, 211, 584(542), 611
- Wurster, C., 273(356), 297, 389(243), 390 (243), 479
- Wyman, L. J., 303(18), 343
- Wynne-Jones, W. F. K., 367(126,127), 368 (126,127), 476, 520(362-364), 558(362-364), 560(362,363), 576(362,364), 607

Y

- Yablokov, Y. V., 121(300), 134
- Yager, W. A., 120(292), 134
- Yagi, H., 322(108), 345, 370(140), 476
- Yagupol'skii, L. M., 491(242), 492(242), 566(242), 568(242), 604
- Yakubovich, A. Ya., 249(194), 263(194), 267(194,322), 269(194), 274(364), 285 (429), 293, 296, 297, 299
- Yale, H. L., 389(246), 479
- Yamada, S., 183(72), 210, 212
- Yamagami, M., 281(410), 298
- Yamagishi, K., 229(77), 289
- Yamakawa, M., 23(69), 65(207), 67(207), 68, 73, 76
- Yamashita, T., 84, 90(76), 126, 128
- Yamazaki, M., 8, 9(14), 68(14), 72
- Yang, M. T., 158(71), 163
- Yang, N. C., 168(18), 180, 209, 210
- Yarborough, V. A., 90(69), 128
- Yarian, D. R., 222(39), 288
- Yarwood, J., 89, 90, 127
- Yasnopol'ski, V. D., 228(65), 289
- Yen, T. F., 304, 305(27), 343
- Yhland, M., 122(303), 124(328), 134, 135, 182(64), 210, 587(547), 611
- Yoffe, A. D., 170(22), 209
- Yokoe, I., 183(72), 210, 212
- Yoneda, S., 332(164), 333(164), 347
- Yonezawa, T., 24(77), 26(77), 29-31(77), 71(231,232), 73, 77
- Yorka, K. V., 426(426), 427(426), 484
- Yoshida, Z., 101(107), 129, 235(106), 290
- Yoshihara, K., 119(276), 133

Young, A., 421(414), 436(414), 438(414),  
442(414), 452(414), 484  
Young, H. L., 284(421), 299  
Young, J. A., 243(158), 292  
Young, J. H., 328(142), 346, 352(17), 473  
Young, R. H., 125(332), 135  
Young, R. P., 119(273), 133  
Yun, B. H., 102(120), 129

## Z

Zabrodina, K. S., 393(276), 399(276), 443  
(276), 471(276), 480  
Zahler, R. E., 490-492, 493(1), 495(1), 505  
(53), 509(53), 510(53), 534(53), 540(1),  
556(1), 565, 568(479), 588(1), 598, 599,  
610  
Zahradnik, A., 145(29), 162  
Zaitsev, P. M., 364(109), 368(128), 373  
(109,128), 476  
Zaitseva, Z. V., 364(109), 373(109), 476  
Zakharkin, L. I., 90(75), 128, 381(203),  
391(203), 398-401(203), 478  
Zaki, A., 574(513), 610  
Zalukaevs, L. P., 412(372,375), 413(372,  
375), 414(375,380), 483  
Zalukajevs, L., 314(66), 344  
Zanetti, G., 174(35), 184(35), 209  
Zavilovitch, I. M., 374(151), 477  
Zbarskii, V. L., 564(471-473), 571(471,  
472), 609  
Zeiger, H. J., 125(342), 135

Zeile, K., 257(238), 294  
Zeldin, L., 414(381), 483  
Zelinsky, N., 383(214), 479  
Zeller, P., 417(392), 422(392), 445(392),  
449(392), 450(392), 483  
Zerevitinov, T., 244(160), 292  
Zhigareva, G. G., 381(203), 391(203),  
398-401(203), 478  
Zhilin, V. F., 564(471-473), 571(471,472),  
609  
Ziegenbein, W., 228(69), 289  
Ziegler, K., 574(510), 610  
Zimmer, H., 153(63,64), 163  
Zimmerman, H., 169, 200(103), 209, 211,  
363(92), 381(92), 475, 583(541), 611  
Zincke, T., 574(509), 610, 614(12), 616  
(12), 681  
Zinin, N., 470(485), 486  
Zirin, M. H., 120(286), 134  
Zita, N., 263(295), 295  
Zlotschenko, S. I., 235(111), 290  
Zollinger, H., 490, 491, 498(36), 501(32-  
37,39,40), 504(32-34,36), 522(34,35), 523  
(34,35,37,40), 524(36), 525(34,36,38),  
528, 529(34-38,40), 530(15,32,34,35), 531  
(15,379-381), 598, 599, 607  
Zondler, H., 582(529,530), 611  
Zonis, E. S., 362(90), 475  
Zubkova, L. B., 115, 133  
Züblin, J., 390(259), 394(259), 397(259),  
480  
Zvika, I., 88(47), 127  
Zyzynski, W., 103(144), 130

# Subject index

## A

- p*-Acetamidonitrobenzene,  $^{15}\text{N}$  chemical shifts in, 111
- Acetone cyanohydrin nitrate, use of as nitrating agent, 315–316
- Acetonitrolic acid, 394, 396
- 1-Acetoxy-1,1-di(*p*-chlorophenyl)-2-nitropropane, 317
- 1-Acetoxy-1,1-diphenyl-2-nitroethane, 317
- threo*-1-Acetoxy-1,2-diphenyl-2-nitroethane, 317
- 1-Acetoxy-2-methyl-2-nitrosopropane, paramagnetic resonance absorption of, 252
- 3 $\beta$ -Acetoxy-17 $\beta$ -nitro-5 $\beta$ -androstandane, 308
- 1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane, 659
- Acetyl nitrate, preparation of, 316  
use of as nitrating agent, 316–318
- m*-Acetylnitrobenzene, electronic absorption spectrum of, 98
- o*-Acetylnitrobenzene, electronic absorption spectrum of, 99
- p*-Acetylnitrobenzene, electronic absorption spectrum of, 97
- 2-Acetyl-2-nitrosopropane, 259  
N=O stretching frequency of, 140
- 1-Acetyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, x-ray diffraction of, 674
- Activating effect, of aromatic nitro group in halogen displacement reactions, 492–494
  - of nitro group in nucleophilic displacement, 489–490
  - of *ortho*-substituents in halonitrobenzenes, 494–498
  - relative order of halogen atoms in halonitrobenzenes, 535
- Activation energies, of methoxydechlorination of chloronitrobenzenes, 494

- Acyclic nitronic acid anhydrides, 461
- Addition–elimination mechanism, in nucleophilic aromatic substitution, 490
- Aliphatic nitro compounds, see also *Nitroalkanes*
  - C–N stretching frequency of, 89
  - electronic spectra of, 35,
  - $^{14}\text{N}$  chemical shifts in, 110
  - preparation of, from secondary ketoximes, 305
- Aliphatic nitroso compounds, absorption
  - maximum of, 147
  - characteristic uv absorption of, 202
  - effect of  $\alpha$ -substituent on N=O stretching frequency, 140
  - formation of nitroxides by irradiation of, 203–205
  - nucleophilicity of, 271–272
  - $n-\pi^*$  transitions of, 147
- Aliphatic C-nitroso compounds, ir
  - absorption of *cis*-dimer, 141
  - ir absorption of *trans*-dimer, 141
- Aliphatic nitroxides, from aliphatic amines, 15,
  - diradicals of, 20–21
  - electronic properties of, 15–22
  - magnetic properties of, 15–22
  - from oximes, 21–22
- C-Alkylation, factors influencing of
  - nitronate salts, 426–430
  - of mercury phenylmethanenitronate, 429
  - of nitronate salts, 417–422
  - of silver dinitromethanenitronate, 428
  - of silver phenylmethanenitronate, 429
- O-Alkylation, factors influencing of
  - nitronate salts, 426–430
  - of nitronate salts, 417–422
  - of silver nitrocyanomethanenitronate, 428



- Alkyl 3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadiene nitronates, decomposition of, 451
- Alkyl fluoroborates, use of in *O*-alkylation of nitronate salts, 417-422
- Alkyl nitrates, in preparation of nitro compounds, 310-314  
reaction of with base, 313
- Alkyl nitrites, O—N=O bending vibrations of *cis* form, 146  
O—N=O bending vibrations of *trans* form, 146
- Alkyl nitrobenzenes, infrared spectra of, 87
- Alkyl nitrobenzoates, electronic absorption spectra of, 103
- 2-Alkyl-2-nitroso-1-indanones, ring expansion of, 259
- Ambident anions, 429
- m*-Aminonitrobenzene, electronic absorption spectrum of, 98
- o*-Aminonitrobenzene, electronic absorption spectrum of, 99
- p*-Aminonitrobenzene, coupling constants of, 109
- p*-electronic absorption spectrum of, 97, 100  
<sup>15</sup>N chemical shifts in, 111  
proton chemical shifts of, 109
- 1-Amino-2-nitrocyclopentanecarboxylic acid, 320
- 1-Amino-5-nitropentane, 328
- Aminonitropyridines, electronic absorption spectra of, 102
- p*-Aminonitrosobenzene, 258
- Amyl 2,2-dimethyl-5-nitrohexanoate, 312
- Amyl 2-methyl-5-nitrohexanoate, 312
- Amyl nitrite, N=O stretching vibration frequency of, 139
- Amyl 10-nitrodecanoate, 312
- Amyl 12-nitrododecanoate, 312
- Amyl 7-nitroheptanoate, 312
- Amyl 6-nitrohexanoate, 312
- Amyl 9-nitrononanoate, 312
- Amyl 8-nitrooctanoate, 311, 312
- Amyl 5-nitropentanoate, 312
- p*-Anilinonitrosobenzene, 280
- Anthrone-10-nitronic acid, 416
- Aristolochic acid, natural occurrence of, 325
- Aromatic nitroamino compounds, electronic absorption spectra of, 102
- Aromatic nitrocarboxylates, nucleophilic displacement of ester group from, 572-573
- Aromatic nitro compounds, see also *Nitroaromatics*  
asymmetric and symmetric stretching frequencies of, 85-88  
C—N stretching frequency of, 89  
electronic absorption spectra of, 94-102  
infrared spectra of, 85-88  
light-catalyzed intramolecular rearrangements of, 185-191  
magnetic properties of, 54-58  
photoinduced nucleophilic substitution of, 200-202  
Raman spectra of, 85-88  
relative leaving abilities for various substituents in nucleophilic displacements of, 543
- Aromatic nitro group, activating effect in halogen displacement reactions, 492-494  
importance of intramolecular hydrogen bonding in, 497
- Aromatic nitrophosphates, nucleophilic displacement of phosphate group from, 572-573
- Aromatic nitroso compounds, amine zwitterions of, 258-259  
formation of nitroxides by irradiation of, 203-205  
magnetic properties of, 54-58  
*n*- $\pi^*$  transitions of, 147-148  
nucleophilicity of, 271-272  
 $\pi$ - $\pi^*$  transitions of, 151  
stabilization of monomer by resonance, 253  
substitution reactions of, 283-284
- Aromatic C-nitroso compounds, ir absorption of *cis*-dimer, 141  
ir absorption of *trans*-dimer, 141

Aromatic nitroso zwitterions, O-acylation of, 258  
 O-alkylation of, 258  
 Aromatic nitrosulfonates, nucleophilic displacement of sulfonate group from, 572-573  
 Aromatic nitroxides, magnetic properties of, 68-69  
 Aromatic nucleophilic substitution, relative activating power of *o*-, *m*-, and *p*-nitro groups, 493  
*α*-Arylazonitronic esters, 424  
 Arylmethanenitronic acids, 398  
   tautomerism of, 354  
 Arylnitromethanes, preparation of by Victor Meyer Reaction, 325, 328  
 Atomic orbitals, of nitric oxide, 8

## B

Bachmann-Knöffler-Eble process, 660  
 Baudisch reaction, preparation of nitroso compounds by, 222-223  
 Benzaldoxime, 458  
 Benzilic rearrangement, of nitro-phenanthra-9,10-quinones, 597  
 Benzonitrolic acid, 396  
 1-Benzoylamino-5-nitropentane, 328  
 Benzoylindenitronic acid, 415  
 2-Benzoyl-2-nitropropane, 259  
*N*-Benzyl-*N*-methylnitrosamine, chemical shifts of, 157  
*N*-Benzyl-*N*-phenylnitrosamine, chemical shifts of, 157  
*N*-Benzyl-*N*-*i*-propylnitrosamine, chemical shifts of, 157  
 Bicyclic nitronic esters, preparation of, 431  
*o*-Biphenylnitrene, 263  
 Bornane-2-nitronic acid, 398  
 1-Bromo-1-chloro-2-nitroethane, 318  
 Bromomethanenitronic acid, 358  
 2-Bromo-2-nitroalkyl amines, infrared spectroscopy in preparation of, 90  
 10-Bromo-10-nitroanthrone, 416  
*m*-Bromonitrobenzene, electronic absorption spectrum of, 98  
*o*-Bromonitrobenzene, electronic absorption spectrum of, 99  
*p*-Bromonitrobenzene, coupling constants of, 109  
   electronic absorption spectrum of, 97  
   <sup>15</sup>N chemical shifts in, 111  
   proton chemical shifts of, 109  
 2-Bromo-2-nitrobornane, 304, 341  
*pseudo*-Bromonitrocampafor, 411  
 1-Bromonitronic esters, 443  
 1-Bromo-1-nitropropane, 335  
*α*-Bromonitrosoalkanes, 393  
*p*-Bromonitrosobenzene, 253, 260, 284  
   *n*- $\pi^*$  absorption data of, 151  
*p*-Bromonitrosobenzene, enthalpies of dimerization of, 150  
   polarographic reduction potentials of, 151  
   N=O stretching frequency of, 140  
   visible absorption data of, 150  
 2-Bromo-2-nitro-1-tetralone, 410  
*o*-Bromophenylcyanomethanenitronic acid, 403  
*p*-Bromophenylcyanomethanenitronic acid, 403  
 4-Bromophenylmethanenitronic acid, 360, 424, 440  
 1,4-Butanebisnitronic acid, intramolecular hydrogen bonding in, 372  
 4-*t*-Butyl cyclohexanenitronate, 363  
*t*-Butyl fluorene-9-nitronate, 379  
*N*-*n*-Butyl-*N*-methylnitrosamine, chemical shifts of, 157  
*N*-*t*-Butyl-*N*-methylnitrosamine, chemical shifts of, 157  
 2-Butylnitrate, *n*- $\pi^*$  transition bands of, 92  
*t*-Butylnitrite, flash photolysis of, 148  
 2-Butylnitrite, *n*- $\pi^*$  transition bands of, 92  
*m*-*t*-Butylnitrobenzene, electronic absorption spectrum of, 98  
*o*-*t*-Butylnitrobenzene, electronic absorption spectrum of, 99  
*p*-*i*-Butylnitrobenzene, electronic absorption spectrum of, 101  
*p*-*t*-Butylnitrobenzene, electronic absorption spectrum of, 97

- 4-*t*-Butyl-1-nitrocyclohexane, equilibrium constant of from nmr spectra, 107
- cis*-4-*t*-Butylnitrocyclohexane, coupling constants of, 108
- nmr spectrum of, 107-108
- $\alpha$ -proton chemical shift in, 107-108
- trans*-4-*t*-Butylnitrocyclohexane, 363
- coupling constants of, 108
- nmr spectrum of, 107-108
- $\alpha$ -proton chemical shift in, 107-108

## C

- m*-Carbethoxynitrobenzene, half-band widths of, 87
- molar extinction coefficients of, 87
- nitro stretching frequencies of, 87
- 2-Carbomethoxybenzalnitrimine, 648
- p*-Carbomethoxynitrobenzene, half-band widths of, 87
- molar extinction coefficients of, 87
- nitro stretching frequencies of, 87
- Carbonyl compounds, preparation of by Nef reaction, 388-389
- m*-Carboxynitrobenzene, electronic absorption spectrum of, 98
- o*-Carboxynitrobenzene, electronic absorption spectrum of, 99
- p*-Carboxynitrobenzene, electronic absorption spectrum of, 97
- Charge-transfer complexes, 531
- spectra of, 116-120
- $\alpha$ -Chloronitroalkanes, mechanism of hydrolysis of, 405
- m*-Chloronitrobenzene, electronic absorption spectrum of, 98
- o*-Chloronitrobenzene, electronic absorption spectrum of, 99
- p*-Chloronitrobenzene, coupling constants of, 109
- electronic absorption spectrum of, 97
- half-band widths of, 87
- molar extinction coefficients of, 87
- $^{15}\text{N}$  chemical shifts in, 111
- proton chemical shifts of, 109
- Chloronitrobenzenes, activation energies of for methoxydechlorination of, 494
- 5 $\alpha$ -Chloro-6 $\beta$ -nitrocholesteryl acetate, 323
- 1-Chloro-2-nitrocyclohexane, 318
- 1-Chloro-1-nitroethane, 335, 405
- 1-Chloro-1-nitroethane-1-*d*, 336
- 4-Chloro-2-nitronitrosobenzene, 461
- 5-Chloro-2-nitronitrosobenzene, 461
- 1-Chloro-1-nitropropane, nitro stretching frequencies of, 82
- 2-Chloro-2-nitropropane,  $^{14}\text{N}$  chemical shifts in, 110
- nitro stretching frequencies of, 82
- 3-Chloro-5-nitrosoacetophenone, 242
- $\alpha$ -Chloronitrosoalkanes, formation of in Nef reaction, 248-249
- p*-Chloronitrosobenzene, 280
- $n\text{-}\pi^*$  absorption data of, 151
- $\text{N}=\text{O}$  stretching frequency of, 140
- polarographic reduction potentials of, 151
- 2-Chloro-2-nitrosobutane, halogen atom expulsion in, 208
- gem*-Chloronitrosocyclohexane, deoxygenation of, 264
- hydrolysis of, 259
- ring-enlargement of, 264
- 1-Chloro-1-nitrosocyclohexane, 248, 252, 270
- $n\text{-}\pi^*$  transition of, 148
- $\pi\text{-}\pi^*$  transition of, 148
- 1-Chloro-2-nitrosocyclohexane,  $\text{N}=\text{O}$  stretching frequency of, 140
- 9-Chloro-10-nitrosodecalin,  $\text{N}=\text{O}$  stretching frequency of, 140
- 1-Chloro-1'-nitrosodicyclohexyl,  $\text{N}=\text{O}$  stretching frequency of, 140
- 2-Chloro-2-nitrosopropane, 252
- $\text{N}=\text{O}$  stretching frequency of, 140
- 1-Chloro-2-nitro-1,1,2,2-tetrafluoroethane, 323
- m*-Chloroperbenzoic acid, use in oxidation of amines, 308
- 4-Chlorophenylmethanenitronic acid, 360
- $\beta$ -Chlorotetrafluoronitrosoethane, dimer of, 255
- Conductivity measurements, of nitroalkanes, 372

- of nitronic acids, 372
- Copper nitronate salts, 460
- Cotton effect, see also *Optical rotatory dispersion*
  - of nitroso compounds, 155
- m*-Cyanonitrobenzene, half-band widths of, 87
  - molar extinction coefficients of, 87
  - nitro stretching frequencies of, 87
- p*-Cyanonitrobenzene, half-band widths of, 87
  - molar extinction coefficients of, 87
  - <sup>15</sup>N chemical shifts in, 111
- $\alpha$ -Cyanonitrosoalkanes, reaction of with dienes, 270–271
- 1-Cyano-1-nitrosocyclohexane, 240
- 2-Cyano-2-nitrosopropane, N=O stretching frequency of, 140
- $\alpha$ -Cyanophenylnitromethane, 466
- Cyclic nitronic acid anhydrides, 461
- Cyclic nitronic esters, mechanism of formation of, 431
  - preparation of, 430–435
  - properties of, 432
  - synthesis of, 432–434
- Cyclododecanenitronic acid, 398
- Cycloheptyl nitrite, photolytic isomerization of, 222
- Cyclohexanenitronic acid, 400
- Cyclohexylnitromethane, nitro stretching frequencies of, 82
- Cyclonite, 649, 676, 678
  - polarization of, 678
  - preparation of, 650
  - x-ray diffraction of, 674
- Cyclonite oxide, 656, 676
- Cyclooctyl nitrite, photolytic isomerization of, 222
- 2,4-Cyclopentadiene-1-nitronic acid, 360
- 1-Cyclopropyl-1,1-dinitroethane, 338
- 1-Cyclopropylnitroethane, preparation of by oxidation of oxime, 307

## D

- Deoxygenation, of aromatic nitro compounds by free radicals, 245
  - intramolecular transfer of oxygen in, 246
- of nitro compounds, 244–248
- of nitroso compounds, 263–264
- 1,9-Diacetoxy-2,6-diacetyl-4,8-dinitro-2,4,6,8-tetrazanonane, 665
- 1,9-Diacetoxymethyl-4-aceto-2,6,8-trinitro-2,4,6,8-tetrazanonane, 664
- 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-tri-azaheptane, 659
- 1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetra-cyclooctane, 667
- Dibenzohydroxamic acid, 464
- 1,5-Dibenzyl-3,7-dinitro-1,3,5,7-tetra-cyclooctane, 651
- Dibenzylideneacetone, electronic absorption spectrum of, 102
- 2,6-Dibromo-4-nitrophenol, coupling constants of, 109
- 2,6-Dibromo-4-nitrosophenol, 226, 227
- Di-*t*-butylnitroxide, ESR spectral properties of, 19
  - UV spectral properties of, 19
- 1,1-Dicarbethoxy-2,3-diphenyl-3-nitro-cyclopropane, 341
- 1,4-Dichloro-1,4-dinitrosocyclohexane, 255
  - N=O stretching frequency of, 140
- 1,1-Dichloro-1-nitroethane, nitro stretching frequencies of, 82
- 3,5-Dichloronitrosobenzene, 253
  - N=O stretching frequency of, 140
- 1,1-Dichloro-1-nitrosoethane, N=O stretching frequency of, 140
- Dicyclohexylnitrosamine, ir bands of, 145
- Dicyclopentylnitrosamine, ir bands of, 145
- Dicyclopropylnitromethane, preparation of by oxidation of oxime, 307
- Diethyl nitromalonate, 315
  - preparation of by oxidation of oxime, 307
- Diethylnitrosamine, electronic absorption spectral data of, 154
  - ir bands of, 145
  - N=O stretching frequency of, 144
- Dihalodinitromethanes, 405

- 2,4-Dihalonitrobenzenes, *ortho*-effects in, 498
- Di-*n*-hexylnitroxide, ESR spectral properties of, 19
- UV spectral properties of, 19
- 3,6-Dihydrooxazine, 249
- 2,5-Dimethoxy-4-hydroxynitrosobenzene, 259
- m*-Dimethylaminonitrobenzene, electronic absorption spectrum of, 98
- o*-Dimethylaminonitrobenzene, electronic absorption spectrum of, 99
- p*-Dimethylaminonitrobenzene, electronic absorption spectrum of, 97
- half-band widths of, 87
- molar extinction coefficients of, 87
- p*-Dimethylaminonitrosobenzene, 252, 253
- enthalpies of dimerization of, 150
- visible absorption data of, 150
- N,N*-Dimethylaniline N-oxide, dipole moment of, 64-65
- Dimethyl 2-chloro-4-nitromethylpentanedioate, 319
- 2,3-Dimethyl-2,3-dinitrobutane, 339
- 1,5-Dimethyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane, 651
- m-N*-Dimethylnitroaniline, electron absorption spectrum of, 49
- o-N*-Dimethylnitroaniline, electron absorption spectrum of, 49
- p-N*-Dimethylnitroaniline, electron absorption spectrum of, 49
- 2-3-Dimethylnitrobenzene, ESR spectrum of, 63
- 2,6-Dimethylnitrobenzene, ESR spectrum of, 63
- 3,5-Dimethylnitrobenzene, ESR spectrum of, 63
- 2,5-Dimethyl-2-nitrocyclopentanone, 312
- Dimethylnitrosamine, chemical shifts of, 157
- electronic absorption spectral data of, 154
- ir bands of, 145
- N=O stretching frequency of, 144
- solvent effects on ir frequencies of, 146
- solvent effects on the  $n-\pi^*$  band of, 153
- N,N*-Dimethylnitrosamine,  $n-\pi^*$  transition of, 148
- Dimethylnitramine, as intermediate in formation of phenylnitramine, 650-654, 656, 658
- Dimethyloxosulfoniumylide, as alkylating agent in nucleophilic displacement of nitroaromatics, 556
- Dimethyl pseudonitrole, 394
- 2,3-Dimethyl-2,4,4-trinitropentane, 338
- $\alpha,\omega$ -Dinitroalkanes, 328
- from  $\alpha,\omega$ -dibromoalkanes with sodium nitrite, 333
- preparation of by cleavage of dinitrocycloalkanones, 311
- preparation of by Victor Meyer reaction, 325
- 1,1-Dinitroalkanes, electronic absorption spectra of, 94
- 1,1-Dinitroalkane salts, uv correlation with electronic effects, 105
- uv correlation with steric effects, 105
- 2,4-Dinitroaniline, electronic absorption spectrum of in liquid ammonia, 104
- 2,6-Dinitroaniline, electronic absorption spectrum of in liquid ammonia, 104
- 3,5-Dinitroaniline, electronic absorption spectrum of in liquid ammonia, 104
- p,p'*-Dinitroazoxybenzene, nitro stretching frequencies of, 85
- Dinitrobenzene, effect of pH electronic absorption spectra of, 104
- m*-Dinitrobenzene, electronic absorption spectrum of, 98
- esr spectra of radical anions of, 122-124
- half-band widths of, 87
- molar extinction coefficients of, 87
- nitro stretching frequencies of, 87
- o*-Dinitrobenzene, esr spectra of radical anions of, 122-123
- p*-Dinitrobenzene, electronic absorption spectrum of, 97, 100

- esr spectra of radical anions of, 122-123
- <sup>15</sup>N chemical shifts in, 111
- nitro stretching frequencies of, 85
- proton chemical shift of, 109
- 1,4-Dinitrobenzene, 426
- ESR spectrum of, 62
- Dinitrobenzene derivatives, electronic absorption spectra of in alkaline solutions, 105-106
- 1,3-Dinitrobenzene derivatives, infrared data of, 90
- Dinitrobenzenes, solvent effects on electronic absorption spectra, 103
- 2-(2,4-Dinitrobenzyl)-pyridine, diffuse reflectance spectroscopy of, 125
- 1,1'-Dinitrobicyclohexyl, 339
- 1,4-Dinitrobutane, 311
- preparation of by modified Victor Meyer reaction, 332
- 2,2-Dinitrobutane, 338
- 1,2-Dinitro-2-butene, 405
- 2,6-Dinitro-4-chlorophenol, coupling constants of, 109
- 7,7-Dinitro-5 $\alpha$ -cholestone, 303
- 1,1-Dinitrocyclohexane, 338
- 1,3-Dinitrocyclohexane, 363
- 1,4-Dinitrocyclohexane, 340, 363
- 2,6-Dinitrocyclohexanone, 311
- $\alpha,\alpha'$ -Dinitrocyclohexanone, 310
- 1,10-Dinitrodecane, preparation of by Victor Meyer reaction, 327
- 3,7-Dinitro-3,7-diaza-1,5-dioxacyclooctane, 650
- 1,3-Dinitro-1,3-diaza-5-oxacyclohexane, polarization of, 678
- 3,5-Dinitro-3,5-diaza-1-oxacyclohexane, 656
- 3,5-Dinitro-3,5-diazapiperidinium nitrate, 657
- 3,5-Dinitro-3,5-diazapiperidylethoxymethane, 657
- 3,5-Dinitro-3,5-diazapiperidylmethyl acetate, 659
- 3,5-Dinitro-3,5-diazapiperidylmethyl-N-hydroxymethylnitramine, from nitrolysis of hexamethylenetetramine, 653
- 1,3-Dinitro-4,6-dinitrosobenzene, 240
- p,p'*-Dinitrodiphenyl, nitro stretching frequencies of, 85
- a,i*-1,2-Dinitro-1,2-diphenylethane, 338
- meso*-1,2-Dinitro-1,2-diphenylethane, 338
- p,p'*-Dinitrodiphenylsulfide, nitro stretching frequencies of, 85
- 3,7-Dinitroendoethylene-1,3,5,7-tetraazacyclooctane, 651
- 1,1-Dinitroethane, 335
- proton chemical shifts in, 107
- 1,2-Dinitroethylene, 405
- 2,4-Dinitrofluorobenzene, 499, 542
- Dinitrogen tetroxide, use as nitrating agent, 319-320
- Dinitrogen trioxide, use as nitrating agent, 320-323
- 2,7-Dinitro-1,7-heptanediol, 372
- 1,6-Dinitrohexane, 311
- preparation of by modified Victor Meyer reaction, 332
- 2,5-Dinitro-1,6-hexanediol, 371
- 4,4-Dinitro-3-hexanone, 320
- cis*-3,4-Dinitro-3-hexene, 320
- trans*-3,4-Dinitro-3-hexene, 320
- 10,10-Dinitro-2-hydroxycamphane, 340
- Dinitroinositol, nmr spectrum of tetra-*o*-acetyl derivative of, 108
- Dinitromethane, nmr of, 38-
- proton chemical shifts in, 107
- 1,1-Dinitro-2-methylpropane, 376
- 1,5-Dinitronaphthalene, electronic absorption spectrum of, 96
- 1,8-Dinitronaphthalene, esr spectrum of, 63
- Dinitronaphthalenes, nmr spectra of, 109
- $\alpha,\alpha'$ -Dinitronic acids, salts of acyclic, 411-412
- 1,1-Dinitro-1-nitrosoethane, 396
- 1,5-Dinitropentane, 311
- 2,4-Dinitrophenol, far ir spectrum of, 113
- 2,6-Dinitrophenol, far ir spectrum of, 113
- 2,4-Dinitrophenyl aryl ethers, *trans*-etherification of with aliphatic alcohols, 568

- 2,4-Dinitrophenylhydrazine, 499  
 2,4-Dinitrophenylhydrazones, electronic absorption spectra of, 102  
 2,4-Dinitrophenylhydrazones, nmr spectra of, 108  
*N*-(2,4-Dinitrophenyl)imidazolium salts, electronic absorption spectra of, 105  
*N*-( $\alpha$ )-2,4-Dinitrophenyl-sulfonylamino acids, electronic absorption spectra of, 102  
*N,N'*-Dinitropiperazine, polarization of, 678  
 1,1-Dinitropropane, 335, 338  
   proton chemical shifts in, 107  
 2,2-Dinitropropane, nitro stretching frequencies of, 82  
 2,2-Dinitro-1,3-propanediol, 338  
 2,2-Dinitropropanol, 335  
 1,2-Dinitroso-4-azido-5-nitrobenzene, 262  
*o*-Dinitrosobenzene, 254, 268  
*p*-Dinitrosobenzene, 239, 254, 279  
 2,2'-Dinitrosobiphenyl, 255  
 4,6-Dinitroso-*N,N'*-dimethyl-*m*-phenylenediamine, from *N,N'*-dinitroso-*N,N'*-dimethyl-*m*-phenylenediamine, 223-224  
 Dinitrosopentamethylenetetramine, electronic absorption spectral data of, 154  
 1,4-Dinitrosopiperazine, *cis* and *trans* isomers in nmr spectrum of, 157  
 2,4-Dinitrosoresorcinol, 226  
 1,2-Dinitro-1,1,2,2-tetrafluoroethane, 319  
 $\alpha,\alpha$ -Dinitrotoluene, 395  
 2,6-Dinitro-4-trifluoromethyl-*N*-methylaniline, photolysis of, 188  
 1,3-Dinitro-1,2,3-triphenylpropane, preparation of by Michael addition, 431  
 1,5-Dinitroxy-2,4-dinitro-2,4-diazapentane, 656  
*N,N'*-Dioxoazomethane, *cis-trans* isomers of, 252  
 Di-*n*-pentylnitrosamine, electronic absorption spectral data of, 154  
 Diphenylcyanonitromethane, 315  
 2,3-Diphenyl-2-cyclopropenyl nitrite, 342  
 1,2-Diphenyl-1,2-dinitrosoethylene, 239  
 Diphenylfuroxan, 239  
 Diphenylmethanenitronic acid, 401  
   preparation of, 351  
 1,2-Diphenyl-3-nitrocyclopropene, 342  
   electronic absorption spectrum of, 102  
 Diphenylnitromethane, 315  
 Diphenylnitroxide, preparation of, 15  
 4,4-Diphenyloxazetidinone, 249  
 $\alpha,\alpha$ -Diphenyl- $\beta$ -picrylhydrazil, esr spectrum of, 120-121  
 1,3-Dipolar addition reactions, of nitronic esters, 453-459  
 Dipole moment, of nitramines, 675-680  
 Dipotassium cyclopentanone-2,5-bisnitronate, 412  
 Dipotassium 1,4-dibromo-1,4-butane-dinitronate, 404  
 Dipotassium tetranitroethane, 397  
*N,N*-Di-*i*-propylnitrosamine, chemical shifts of, 157  
 Di-*n*-propylnitrosamine, electronic absorption spectral data of, 154  
 Di-*i*-propylnitrosamine, ir bands of, 145  
 DPT, 651

## E

- Ehrlich-Sachs reaction, of nitroso compounds, 277-278  
 Electrical polarization, of nitamines, 675-680  
   of polynitrimines, 675-680  
 Electron absorption spectra, of di-*t*-butylnitroxide, 19  
   of di-*n*-hexylnitroxide, 19  
   of *m*-*N*-dimethylnitroaniline, 49  
   of *o*-*N*-dimethylnitroaniline, 49  
   of *p*-*N*-dimethylnitroaniline, 49  
   of isoquinoline N-oxide, 66-68  
   of nitramide, 35  
   of nitrobenzene, 42-43  
   of nitroethylene, 39  
   of nitropropene, 37  
   of 1-nitro-1-propene, 39

- of 2-nitro-1-propene, 39
- of 3-nitro-1-propene, 39
- of pyridine N-oxide, 65-66
- of stable nitroxides, 19
- Electron diffraction, studies on nitro-methane, 32
- studies on nitrotribomomethane, 32
- studies on nitrotrifluoromethane, 32
- Electronic absorption spectra, acid-base equilibria in, 104-105
- of anions, 105-106
- of aromatic nitro compounds, 94-102
- of heterocyclic nitro compounds, 94-102
- hydrogen bonding in, 103
- mesomeric interactions in, 96, 100
- of nitroalkanes, 92-94
- of nitro olefins, 92-94
- of nitrosamines, 152-155
- of nitroso compounds, 147-155
- of C-nitroso compounds, 148-152
- solvent effects in, 103-104
- steric interactions in, 96, 100
- Electronic absorption spectroscopy, inter-action of aromatic nitro com-pounds by, 106
- Electronic properties, of aliphatic nitroxides, 15-22
- of nitroalkanes, 32-38
- of substituted nitrobenzenes, 49-51
- Electronic spectra, of aliphatic nitro compounds, 35
- of nitrobenzene, 42-48
- of nitromethane, 34-35
- of nitropropene, 37
- of nitrosoalkanes, 11-15
- Electronic structure, of nitrobenzene, 39-48
- of nitrogen dioxide, 23-32
- of nitromethane, 32-34
- of nitrosobenzene, 51-54
- Electron spin resonance spectra, of nitro compounds, 120-125
- of nitroso compounds, 160
- Electron spin resonance spectroscopy, of aliphatic nitroxide diradicals, 20-21
- of aliphatic nitroxides, 17-19
- of di-*t*-butylnitroxide, 19
- of di-*n*-hexylnitroxide, 19
- of 2,3-dimethylnitrobenzene, 63
- of 2,6-dimethylnitrobenzene, 63
- of 3,5-dimethylnitrobenzene, 63
- of 1,4-dinitrobenzene, 62
- of 1,8-dinitronaphthalene, 63
- of 2-methylnitrobenzene, 63
- of 4-methylnitrobenzene, 63
- of nitroalkane radical anions, 37-38
- of 4-nitroaniline, 62
- of nitroaromatic radical anions, 58-64
- of *o*-nitrobenzaldehyde, 63
- of *p*-nitrobenzaldehyde, 63
- of nitrobenzene, 62
- of nitroethane, 37-38
- of nitrogen dioxide, 32
- of nitrosobenzene, 64
- of 2,3,5,6-tetramethylnitrobenzene, 63
- of 1,4,5,8-tetranitronaphthalene, 63
- Electrophilic addition reactions, of nitronic acids, 393-398
- Electrophilic substitution, in aromatic systems, 488
- Elimination-addition mechanism, in nucleophilic aromatic substitu-tion, 490
- 1,5-Endoethylidene-3,7-dinitro-1,3,5,7-tetrazacyclooctane, 651
- 1,5-Endomethylene-3,7-diaceto-1,3,5,7-tetrazacyclooctane, 665
- 1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetrazacyclooctane, 651
- 1,5-Endomethylene-3,7-dinitroso-1,3,5,7-tetrazacyclooctane, from hexa-methylenetetramine and nitrous acid, 668-669
- Ethane-1,2-dinitramine, x-ray diffraction of, 674
- trans*-Etherification, see *Nucleophilic displacements*
- Ethyl acetamidomethanenitronate, 438, 443
- Ethyl butane-2-nitronate, 438
- Ethyl carbethoxymethanenitronate, 442
- Ethyl  $\alpha,\alpha$ -dinitrobutyrate, 339
- N*-Ethyl-*N*-methylnitrosamine, chemical shifts of, 157



- Ethyl nitrite, *cis-trans* ratio in, 139  
 Ethyl nitroacetate, 306  
*o*-Ethylnitrobenzene, nitro stretching frequencies of, 85  
*p*-Ethylnitrobenzene, electronic absorption spectrum of, 101  
 Ethyl nitrobenzoates, electronic absorption spectra of, 102  
 Ethyl 2-nitrobutyrate, nitro stretching frequencies of, 82  
 Ethyl  $\alpha$ -nitrocaproate, preparation of by modified Victor Meyer reaction, 332  
 Ethyl  $\alpha$ -nitropropionate, preparation of by Victor Meyer reaction, 327  
 Ethyl  $\alpha$ -phenyl- $\alpha$ -nitroacetate, preparation of by modified Victor Meyer reaction, 332  
*N*-Ethyl-*N*-phenylnitrosamine, chemical shifts of, 157

## F

- Ferroverdin, 251  
 Fischer-Hepp reaction, preparation of nitroso compounds by, 223-225  
 Fluorene-9-nitronic acid, 360, 379, 382  
   bimolecular coupling products of, 402-403  
   mechanism of bimolecular reaction of, 402-403  
 1-Fluoro-2,4-dinitrobenzene, nmr spectrum of, 109  
 Fluoronitroacetyl chloride, 324  
*m*-Fluoronitrobenzene, electronic absorption spectrum of, 98  
*o*-Fluoronitrobenzene, electronic absorption spectrum of, 99  
*p*-Fluoronitrobenzene, electronic absorption spectrum of, 97  
   esr spectra of radical anions of, 122-123  
 $^{15}\text{N}$  chemical shifts in, 111  
 1-Fluoro-5-nitropentane, preparation of by Victor Meyer reaction, 327  
*p*-Fluoronitrosobenzene,  $\text{N}=\text{O}$  stretching frequency of, 140  
*m*-Formylnitrobenzene, electronic absorption spectrum of, 98

- o*-Formylnitrobenzene, electronic absorption spectrum of, 99  
*p*-Formylnitrobenzene, electronic absorption spectrum of, 97  
 Franchimont test, use for detection of nitramines, 622, 638, 649

## G

- Geometry, of nitrobenzene, 39-40  
 of nitrogen dioxide, 23-24

## H

- Hale process, see *Cyclonite*  
 $\alpha$ -Halonitroalkanes, 393  
   coupling of with nitronate salts, 405-406  
 Halonitroaromatics, nucleophilic photochemical displacement of halogen from, 585-586  
 Halonitrobenzenes, activating effects of ortho-substituents in, 494-498  
   deactivation factors of halogen in nucleophilic displacements, 538-539  
   displacement reactions of in nucleophilic substitution, 492-518  
 Hammett  $\rho$ -values in nucleophilic displacements of halogen from, 534  
   influence of carbonyl group in nucleophilic displacements of, 537  
   influence of polarizability on in nucleophilic displacements, 549  
   nucleophilic displacements from, by alkoxy- and phenoxy anions, 512  
   by amines, 499-506  
   by azide and thiocyanate anions, 515  
   by carbanions, 515-516  
   by hydroxide or water, 507-512  
   by mercaptide and thiophenolate anions, 515  
   by sulfide, 514  
   by sulfite, carboxylate, and thio-sulfone, 516-517  
   nucleophilic displacements of halogen from, by halogen, 512-514

- relative order of activating power of halogen atoms in, 535
- relative rates of displacement of halogen from in nucleophilic displacements, 544-545
- relative reactivities for various nucleophiles with in nucleophilic displacements, 547, 548
- substituent effects in nucleophilic reagents correlated by the Hammett equation in nucleophilic displacements in, 551
- o*-Halonitrobenzenes, nucleophilic displacements from by methoxide ions, 536
- $\alpha$ -Halonitronic acids, nucleophilic displacement reactions of, 404-405 reactions of, 404-406
- $\alpha$ -Halonitrosoalkanes, reaction of with dienes, 270-271
- Hammett equation, 551
- Hammett  $\sigma$  constants, correlation of electronic absorption bands with, 100
- Hammett  $\rho$ -values, in nucleophilic displacements of halogen from halonitrobenzenes, 534
- Henry condensation, 378
- 1,1,1,2,2,3,3-Heptafluoro-5-nitropentane, 386
- Heptafluoro-1-nitrosopropane,  $\text{N}=\text{O}$  stretching frequency of, 140
- Heterocyclic nitro compounds, asymmetric and symmetric stretching frequencies of, 85-88
- electronic absorption spectra of, 94-102
- infrared spectra of, 85-88
- nucleophilic displacements in, 581-582
- Raman spectra of, 85-88
- Hexafluorodimethyl-*gem*-nitroschloromethane, 237
- Hexafluorodimethyl-*gem*-nitrosofluoromethane, 240
- 1,6-Hexanebisnitronic acid, intramolecular hydrogen bonding in, 375
- Hexanitroethane, 397
- HMX, 657, 671, polymorphism of, 674, 678-679
- Hydrogen bonding, spectroscopy of, 112-116
- m*-Hydroxynitrobenzene, electronic absorption spectrum of, 98
- o*-Hydroxynitrobenzene, electronic absorption spectrum of, 99
- p*-Hydroxynitrobenzene, electronic absorption spectrum of, 97
- 2-Hydroxy-1-nitropropane, nitro stretching frequencies of, 82
- 2-Hydroxy-3-nitroso-4-aminopyridine, 265
- 2-Hydroxypyridine, dissociation of in electronic absorption spectroscopy, 105

## I

- Indene-1-nitronic acid, 360
- Inductive effects, on rate of proton removal of nitroalkanes, 367-370 on tautomerization rates of nitronic acids, 359-360
- Infrared spectra, of aromatic nitro compounds, 85-88
- of heterocyclic nitro compounds, 85-88
- of nitramines, 671-673
- of *N*-nitroamides, 88
- of nitroamines, 88
- of nitrobenzene, 70
- of *N*-nitrocarbamates, 88
- of nitro compounds, 69, 80-91
- of nitroguanidines, 88
- of  $\alpha$ -nitroketones, 88
- of nitro-olefins, 84
- of nitro salts, 88-89
- of nitroso compounds, 69, 138-147
- of nitroureas, 88
- of polynitroamines, 88
- Infrared spectroscopy, influence of solvents on nitro compounds, 91
- quantitative analysis by, 90
- study of organic reactions by, 90
- Intermediate complexes, nature of in nucleophilic displacements, 531-536

Intramolecular hydrogen bonding, in  
 formation of Meisenheimer com-  
 plexes with amines, 569-570  
 importance of in *ortho* nitro groups,  
 497  
 in nucleophilic displacements of  
 fluoronitrobenzenes, 529-530  
*m*-Iodonitrobenzene, electronic absorp-  
 tion spectrum of, 98  
*o*-Iodonitrobenzene, electronic absorp-  
 tion spectrum of, 99  
*p*-Iodonitrobenzene, electronic absorp-  
 tion spectrum of, 97  
 9-Iodo-9-nitrofluorene, 402  
*o*-Iodonitrosobenzene, enthalpies of  
 dimerization of, 150  
 N=O stretching frequency of, 140  
 visible absorption data of, 150  
*p*-Iodonitrosobenzene, 253  
 enthalpies of dimerization of, 150  
 $n-\pi^*$  absorption data of, 151  
 N=O stretching frequency of, 140  
 polarographic reduction potentials of,  
 151  
 visible absorption data of, 150  
 Ionization constants, of nitroalkanes,  
 372-376  
 of nitronic acids, 372-376  
 Isoquinoline N-oxide, electron absorp-  
 tion spectrum, 66-68  
 Isotope effects, in nitroalkanes, 365  
 in nucleophilic displacements of  
 nitroaromatics, 530-531  
 Isoxazolidines, preparation of from  
 nitronic esters, 454-457  
 2-Isoxazoline N-oxides, see also *Cyclic*  
*nitronic esters*  
 preparation of from 1,3-dinitro-  
 alkanes, 430-431  
 preparation of from 3-halo-1-nitro-  
 alkanes, 430-431  
 Isoxazoline synthesis, mechanism of  
 formation of, 431

## K

Kaplan-Schechter reaction, mechanism  
 of, 336-337

preparation of polynitro compounds  
 by oxidative nitration, 336-339  
 4-Keto-1,1-dinitropentane, 431  
 Keto-enol equilibria, spectroscopy of,  
 112-116  
 Ketonitronic acids, reactions of, 406-417  
 $\alpha$ -Ketonitronic esters, acid-catalyzed  
 hydrolysis of, 440-441  
 hydrogenation of to amino alcohols,  
 444  
 preparation of by Michael addition,  
 414-415  
 tautomerism of, 406  
 uv spectra of, 436  
 4-Keto-1-nitroolefins, preparation of by  
 nitrovinylolation reaction, 414-415  
 Kinetics, of nucleophilic substitution,  
 518-554

## L

Lead  $\alpha$ -cyanophenylmethanenitronate,  
 378  
 Liebermann's test, 273  
 Linear combinations of atomic orbitals,  
 discussion of, 4-6, 533  
 semiempirical calculations of, 6-7  
 Lithium propane-2-nitronate, C-alkyla-  
 tion of, 427  
 O-alkylation of, 427

## M

Magnetic properties, of aliphatic  
 nitroxides, 15-22  
 of aromatic nitro compounds, 54-58  
 of aromatic nitroso compounds, 54-58  
 of aromatic nitroxides, 68-69  
 Mechanism, of nucleophilic substitution,  
 518-554  
 Meisenheimer complexes, 519, 531, 533,  
 557  
 formation of by intramolecular hydro-  
 gen bonding with amines, 569-570  
 importance of in two-step nucleo-  
 philic displacements, 520  
 in nucleophilic displacement of hydro-  
 gen, 554

- in reaction of polynitroaromatics with diazomethane, 595
- in Smiles rearrangement, 588
- in trans-etherification reactions, 565
- Meisenheimer compounds, visible spectra of, 106
- Mercury methanenitronate, 460
- Mercury nitronate salts, 460
- Mercury phenylmethanenitronate, C-alkylation of, 429
- Mesitylnitrimine, 646
- Mesomeric interactions, in electronic absorption spectra, 96, 100
- Methanenitronic acid, 358, 360
- m*-Methoxynitrobenzene, electronic absorption spectrum of, 98
- o*-Methoxynitrobenzene, electronic absorption spectrum of, 99
- p*-Methoxynitrobenzene, coupling constants of, 109
  - electronic absorption spectrum of, 97
  - half-band widths of, 87
  - molar extinction coefficients of, 87
  - <sup>15</sup>N chemical shifts in, 111
  - proton chemical shifts of, 109
- 2-Methoxy-1-nitrobutane, nitro stretching frequencies of, 82
- o*-Methoxynitrosobenzene, N=O stretching frequency of, 140
- p*-Methoxynitrosobenzene, N=O stretching frequency of, 140
- Methyl acetamidomethanenitronate, 443
- Methyl 2-chloro-3-nitropropionate, 319
- 4-Methylcinnoline-1,2-dioxide, 255
- Methyl  $\alpha$ -cyanophenylmethanenitronate, 443
- Methyl dicarbomethoxymethanenitronate, 442, 452
- N*-Methyl-2,6-dinitroaniline, conformation of from nmr spectra, 109
- Methyl dinitromethanenitronate, 453
- Methyl 3,3-dinitropropionate, 338
- Methylene-*bis*-1-(3,5-dinitro-1,3,5-triazacyclohexane), 658
- Methyl 2-hydroxy-3-nitropropionate, 319
- Methylnitramine, Mannich-type reaction of, 623
- N*-Methylnitramino-*bis*-ethane, polarization of, 678
- Methyl nitrite, *cis-trans* ratio in, 139
  - N=O stretching vibration frequency of, 139
  - n*- $\pi^*$  transition of, 148
- Methyl 3-nitroacrylate, 319
- m*-Methylnitrobenzene, electronic absorption spectrum of, 98
- o*-Methylnitrobenzene, electronic absorption spectrum of, 99
- p*-Methylnitrobenzene, electronic absorption spectrum of, 97, 101
- 2-Methylnitrobenzene, esr spectrum of, 63
- 4-Methylnitrobenzene, esr spectrum of, 63
- 2-Methyl-2-nitrobutane, nitro stretching frequencies of, 82
- 3-Methyl-1-nitrobutane, preparation of by Victor Meyer reaction, 327
- cis*-4-Methylnitrocyclohexane, coupling constants of, 108
  - nmr spectrum of, 107-108
  - $\alpha$ -proton chemical shift in, 107-108
- 3-Methyl-3-nitroheptane, 341
- 2-Methyl-2-nitro-3-hydroxybutane, nitro stretching frequencies of, 82
- Methyl nitromethanenitronate, 458
- Methylnitronaphthalenes, pmr spectra of, 109
- Methyl nitronic esters, preparation of by reaction of nitronic acids with diazomethane, 423-424
- Methyl 4-nitrophenylmethanenitronate, 437
- 2-Methyl-2-nitropropanal, 318
- 2-Methyl-1-nitropropane, preparation of by Victor Meyer reaction, 327
- 2-Methyl-2-nitropropane, <sup>14</sup>N chemical shifts in, 110
  - nitro stretching frequencies of, 82
  - n*- $\pi^*$  transition bands of, 93
- 2-Methyl-2-nitro-1-propanol, nitro stretching frequencies of, 82
- 2-Methyl-1-nitropropene, nitro stretching frequencies of, 84

- 2-Methyl-3-nitropropene, nitro stretching frequencies of, 84
- o*-Methylnitrosobenzene, N=O stretching frequency of, 140
- p*-Methylnitrosobenzene, N=O stretching frequency of, 140
- Methyl *o*-nitrosobenzoate, 246  
photolysis of, 286
- 2-Methyl-2-nitrosobutane, ir absorption of *cis* dimer of, 143  
ir absorption of *trans* dimer of, 143
- 2-Methyl-2-nitroso-3-butanone, enthalpies of dimerization of, 150  
visible absorption data of, 150
- 4-Methyl-4-nitroso-2-pentanone, 242
- 1-Methyl-1-nitrosopropane, solvent effects on uv spectrum of *cis* dimer of, 150  
solvent effects on uv spectrum of *trans* dimer of, 150
- 2-Methyl-1-nitrosopropane, ir absorption of *cis* dimer of, 143  
ir absorption of *trans* dimer of, 143  
solvent effects on uv spectrum of *cis* dimer of, 150  
solvent effects on uv spectrum of *trans* dimer of, 150
- 2-Methyl-2-nitrosopropane, 242, 270  
ir absorption of *trans* dimer of, 143  
N=O stretching frequency of, 140  
solvent effects on uv spectrum of *trans* dimer of, 150
- Methyl phenylmethanenitronate, 458
- N*-Methylphenylnitramine, Raman spectrum of, 670
- N*-Methyl-*N*-*i*-propylnitrosamine, chemical shifts of, 157
- Methyl sulfate, alkylating agent for preparation of nitronic esters, 422
- Methyl thionitrite, N=O stretching vibration frequency of, 139
- Methyl 4-toluenesulfonylmethanenitronate, 451
- N*-Methyl-2,4,6-trinitroaniline, conformation of from nmr spectra, 109
- Michael addition, 430  
preparation of 1,3-dinitro-1,2,3-triphenylpropane by, 431  
preparation of  $\gamma$ -ketonitronic acids by, 414-415
- Microwave spectra, of nitrobenzene, 106  
of nitromethane, 106  
of nitromethane-*d*<sub>3</sub>, 106  
of nitroso compounds, 161
- Molecular orbitals, 533  
discussion of, 4-6  
of nitric oxide, 8-10  
of nitrobenzene, 40-42  
of nitrogen dioxide, 25-32  
of nitromethane, 32-34  
semiempirical calculations of, 6-7
- ## N
- 1-Naphthylnitromethane, 314
- Nef reaction, 354, 371, 438, 440, 444, 445, 464  
by direct acid-catalysis, 385-386  
effect of electron-withdrawing groups on inhibition of, 386  
effect of hydrogen bonding on inhibition of, 386  
effect of resonance stabilization on inhibition of, 386  
hydrolysis of *aci*-nitroalkanes by, 248
- Nef reaction, mechanism of, 385  
nitrile oxide mechanism for formation of hydroxamic acids, 389-390  
nitroso alcohol mechanism for formation of hydroxamic acids, 390  
preparation of nitroso compounds by, 248-249  
synthesis of carbonyl compounds by, 388-389
- NENO, preparation of, 639-640
- p*-Neopentylnitrobenzene, electronic absorption spectrum of, 101
- Nitramide, electron absorption spectrum of, 35
- Nitramine, nmr spectrum of, 674  
in preparation of nitrimines, 647  
Raman spectrum of, 671
- Nitramines, see also *Primary nitramines* and *Secondary nitramines*  
deformation vibrations of, 90

- dipole moment of, 675-680
- electrical polarization of, 675-680
- ir spectra of, 671-673
- nitro stretching frequencies of, 88
- physical properties of, 670-680
- Raman spectra of, 670-673
- uv spectra of, 673
- vibrational spectra of, 670-673
- x-ray diffraction of, 674
- Nitramino group, electronic absorption of, 617-618
  - infrared absorption of, 618
- 3-Nitramino-2-nitro-2-azapropylamine nitrate, 658
- 2-Nitramino-5-nitrothiazole, 621
- Nitrates, nitro stretching frequencies of, 88
- Nitrene formation, from nitroso compounds, 263
- Nitric acid, use of as nitrating agent, 323-324
- Nitric oxide, atomic orbitals of, 8
  - molecular calculations of, 7-10
  - molecular orbitals of, 8-10
  - NO stretching frequencies of, 138
- Nitrile oxide mechanism, 441, 442, 459
  - for formation of hydroxamic acids in Nef reaction, 389-390
- Nitrimides, isomerization of to primary nitramides in alkali, 641-643
- Nitrimines, 645-649
  - aqueous hydrolysis of, 648-649
  - isomerization of to nitramines, 646
  - preparation of from chloronitramines, 647-648
  - preparation of from furfural and nitramine, 647
  - preparation of from nitric oxide and diazoalkanes, 648
  - preparation of from oximes and nitrous acid, 645-646
  - reaction of with fuming hydrochloric acid, 646
  - reduction of, 646-647
- 2-Nitriminoimidazolidine, hydration of, 644
  - reaction of with acetyl chloride, 642-643
- 2-Nitrimino-1,3-imidazolidine, 641
- 2-Nitriminooxazolidone, 643
- Nitrite ion, nucleophilicity of, 325
- $\alpha$ -Nitroacetaldoxime, 445
- m*-Nitroacetanilide, electronic absorption spectrum of in liquid ammonia, 104
  - nitro stretching frequencies of, 85
- o*-Nitroacetanilide, electronic absorption spectrum of in liquid ammonia, 104
  - nitro stretching frequencies of, 85
- p*-Nitroacetanilide, electronic absorption spectrum of in liquid ammonia, 104
  - nitro stretching frequencies, 85
- $\beta$ -Nitro acetates, preparation of, 317
- $\alpha$ -Nitroacetone, 407
- $\alpha$ -Nitroacetophenone, 318, 407
- $\omega$ -Nitroacetophenone, 321
  - preparation of by oxidation of oxime, 307
- $\omega$ -Nitroacetophenone oxime, 321
- 1-Nitro-2-acetoxy-2-phenylpropane, 317
- Nitroacridine derivatives, infrared data of, 90
- 1-Nitroadamantane, 340
- $\beta$ -Nitroalcohols, infrared studies of, 112
- $\alpha$ -Nitroaldehyde hydrazones, 397
- Nitroalkanes, see also *Aliphatic nitro compounds*
  - acid-catalyzed halogenation of, 371
  - acid strength of, 364
  - base-catalyzed proton removal from, 365
  - conversion of primary to hydroxamic acids, 389
  - effect of acid-base equilibria on electronic absorption spectra, 104
  - effect of induction on rate of proton removal from, 367-370
  - effect of stereochemistry on rate of proton removal from, 367-370
  - electronic absorption spectra of, 92-94
  - electronic properties of, 32-38
  - formation of carboxylic acids from, 371, 390-391

Nitroalkanes (*continued*)

- formation of hydroxamic acids from, 371
  - ionization constants of, 353, 372-376
  - isotope effect of, 365
  - kinetics of proton removal from, 365
  - $^{14}\text{N}$  hyperfine coupling constants of in radical anions, 121
  - nmr spectroscopy of, 38
  - $n-\pi^*$  transition of, 167
  - optical rotatory dispersion of, 37
  - oxidative dimerization of secondary, 339
  - $\pi-\pi^*$  transition of, 167
  - $pK_a$  of, 373-376
  - preparation of primary by Victor Meyer reaction, 325-327
  - proton chemical shifts in, 107
  - proton removal from, 364-372
    - by acid catalysis, 370
  - radical anions of, 37-38
  - rates of ionization of, 366
  - rates of neutralization of, 368-369
  - reactions of with aminals to amides, 451
  - reaction of with amines, 460-461
  - reaction of with ammonia, 460-461
  - reaction of with diazonium salts, 397-398
  - uv absorption spectra of, 167
- $\beta$ -Nitroalkyl iodides, 320
- N*-Nitroamides, infrared spectra of, 88
- 4-Nitro-4'-amino-diphenylmethane,  
uv spectrum of, 113
- 5-Nitro-2-aminothiazole, by nitration of 2-aminothiazole, 621
- 17 $\beta$ -Nitro-5 $\alpha$ -androstane, 303
- 6 $\alpha$ -Nitro- $\Delta^4$ -androstene-3,17-dione, 324
- 6 $\beta$ -Nitro- $\Delta^4$ -androstene-3,17-dione, 324
- p*-Nitroanilide derivatives, electronic absorption spectra of, 103
- m*-Nitroaniline, nitro stretching frequencies of, 85
- o*-Nitroaniline, electronic absorption spectrum of in liquid ammonia, 104
- nitro stretching frequencies of, 85

- p*-Nitroaniline, electronic absorption spectrum of in liquid ammonia, 104
- equilibria of in sodium hydroxide spectrophotometrically, 104
- esr spectra of radical anions of, 122-123
- esr spectrum of, 62
- $^{15}\text{N}$  chemical shifts in, 110
- nitro stretching frequencies of, 85
- nmr spectra of, 109
- p*-Nitroaniline derivatives, solvent effects on electronic absorption spectra, 103
- Nitroanilines, intermolecular hydrogen bonding in, 113
- uv spectra of, 113
- aci*-Nitroanions, nmr spectra of, 107
- p*-Nitroanisole, esr spectra of radical anions of, 122-123
- intermolecular hydrogen bonding in, 114
- nitro stretching frequencies of, 85, 87
- 9-Nitroanthracene, photolysis of, 179-181
- Nitroanthracenes, nucleophilic displacement reactions of, 579
- Nitroanthranilic acid derivatives, electronic absorption spectra of, 102
- 10-Nitro-9-anthrol, 416
- 10-Nitroanthrone, 416
- 10-Nitro-9-anthryl acetate, 416
- 10-Nitro-9-anthryl benzoate, 416
- Nitroaromatics, see also *Aromatic nitro compounds*
- nucleophilic displacement of alkoxy and aryloxy groups by amines in, 569-572
  - nucleophilic displacement of alkoxy and aryloxy groups by mercaptides in, 571
  - nucleophilic displacement of alkoxy groups in hydrolysis and transesterification of, 565-568
  - nucleophilic displacement of amino and ammonium groups from, 574-575

- nucleophilic displacement of aryloxy groups in hydrolysis and transesterification of, 565-568
- nucleophilic displacement of hydrogen in, 554-561
- nucleophilic displacement of nitro groups in, 561-565
- nucleophilic photochemical displacement of alkoxy groups in, 582-585
- nucleophilic photochemical displacement of nitro groups from, 586-587
- rearrangement reactions of, 587-598
- Smiles rearrangement of, 587-591
- in von Richter reaction, 591-595
- 4-Nitroazoxybenzene, electronic absorption spectrum of, 102
- Nitrobarbituric acid, 413
- o*-Nitrobenzaldehyde, esr spectrum of, 63
  - mechanism of intermolecular oxidation-reduction of, 187-189
  - mechanism of intramolecular oxidation-reduction of, 185-187
  - nitro stretching frequencies of, 85
  - photolysis of, 174
- p*-Nitrobenzaldehyde, 333, 440
  - esr spectra of radical anions of, 122-124
  - esr spectrum of, 63
  - nitro stretching frequencies of, 85
- Nitrobenzaldehydes, chemical shifts in, 110
- p*-Nitrobenzamide, half-band widths of, 87
  - molar extinction coefficients of, 87
  - nitro stretching frequencies of, 87
- N*-Nitrobenzamides, electronic absorption spectra of, 102
- Nitrobenzanthrone, dissociation of in electronic absorption spectroscopy, 105
- Nitrobenzene, 202
  - bond lengths of, 39-40
  - C-N stretching vibration of, 89
  - dipole moment of, 42
  - effect of pH on electronic absorption spectra on, 104
  - electron absorption data of, 95-96
  - electron absorption spectrum of, 42-43
  - electron absorption spectrum of radical anion of, 105
  - electronic spectrum of, 42-48,
  - electronic structure of, 39-48
  - esr spectra of radical anions of, 122-123
  - esr spectrum of, 62
  - geometry of, 39-40
  - infrared spectrum of, 70
  - ionization potential of, 42
  - irradiation of to radical anion, 191-192
  - mechanism of photolysis of, 173
  - microwave spectrum of, 106
  - molecular orbitals of, 40-42
  - <sup>15</sup>N chemical shifts in, 110
  - nitro group participation in photocycloaddition of, 192-199
  - n*- $\pi^*$  transitions of, 45
  - photolysis of, 173
  - physical properties of, 39-48
  - $\pi$ - $\pi^*$  transitions of, 43-44
  - Raman spectrum of, 70
  - skeletal and deformation vibrations of, 89-90
  - solvent effect on electronic absorption spectra, 103
  - solvent effect on pmr spectra of, 111
  - solvent red shifts of, 103
  - x-ray measurements of, 39
- Nitrobenzene derivatives, electronic absorption spectra of in alkaline solutions, 105-106
- Nitrobenzenes, rates of nucleophilic displacement base catalysis reactions of substituted with amines, 522-527
  - solvent effect on pmr spectra of, 111
  - solvent effects on esr spectra of, 123-124
- p*-Nitrobenzenesulfonic acid, half-band widths of, 87
  - molar extinction coefficients of, 87
  - nitro stretching frequencies of, 87
- Nitrobenzenesulfonyl guanidines, in Smiles rearrangement, 590



- p*-Nitrobenzoic acid, half-band widths of, 87  
molar extinction coefficients of, 87  
nitro stretching frequencies of, 85, 87  
Nitrobenzoic acids, electronic absorption spectra of, 102  
*p*-Nitrobenzonitrile, nitro stretching frequencies of, 85, 87  
*p*-Nitrobenzyl alcohol, 333  
*p*-Nitrobenzyl bromide, 333  
*m*-Nitrobenzyl chloride, photolysis of to radical anion, 192  
4-Nitrobenzyl chloride, 426  
1-Nitrobicyclo(3.2.1)cyclooctane, 306  
1-Nitrobicyclo(2.2.1)heptane, 340  
2-Nitrobicyclo(2.2.1)heptane, 341  
*o*-Nitrobiphenyl, conversion into phenanthridine, 379  
nitro stretching frequencies of, 85  
2-Nitrobiphenyl, bathochromic shift in, 101  
Nitrobiuret, decomposition of in aqueous alcohol, 626  
2-Nitrobornane, 304, 424  
*p*-Nitrobromobenzene, nitro stretching frequencies of, 85  
1-Nitrobutane,  $^{14}\text{N}$  chemical shifts in, 110  
 $^{14}\text{N}$  hyperfine coupling constants in radical anions of, 121  
nmr of, 38  
preparation of by Victor Meyer reaction, 327  
proton chemical shifts in, 107  
2-Nitrobutane, 308, 329, 367  
 $^{14}\text{N}$  hyperfine coupling constants in radical anions of, 121  
nitro stretching frequencies of, 82  
 $n-\pi^*$  transition bands of, 92  
preparation of by oxidation of oxime, 307  
preparation of by Victor Meyer reaction, 327  
3-Nitro-2-butanone, 316, 318  
4-Nitro-2-butanone, preparation of by modified Victor Meyer reaction, 332  
2-Nitro-2-butene, 362  
2-Nitro-3-butene, 362  
4-Nitrobut-1-ene, 332  
 $\alpha$ -Nitrobutyrophenone, 314  
1-Nitrocamphene, 341  
 $\omega$ -Nitrocamphene, 321  
 $\alpha$ -Nitrocamphor, mutarotation of, 411  
3-Nitrocamphor, 315  
*N*-Nitrocarbamates, infrared spectra of, 88  
2-Nitro-2-carbethoxyindane-1,3-dione, 314  
1-Nitro-2-chloroalkanes, from nitril chloride and unsymmetrical terminal olefins, 318  
*p*-Nitrochlorobenzene, nitro stretching frequencies of, 85, 87  
4 $\alpha$ -Nitro-5 $\beta$ -cholestane, 303  
4 $\beta$ -Nitro-5 $\alpha$ -cholestane, 303  
6-Nitrocholesteryl acetate, 323  
Nitro compounds, see also *Aliphatic nitro compounds* and *Aromatic nitro compounds*  
*cis-trans* photoisomerization of, 175  
C—N stretching vibration of, 89–90  
esr spectra of, 120–125  
hydrogen abstraction in photolysis of, 181–185  
infrared spectra of, 80–91  
mechanism of hydrogen abstraction in photolysis of, 181–185  
mechanism of modified Victor Meyer reaction, 330–332  
nitro group participation in photocycloaddition of, 192–199  
olefin photocycloaddition of, 176–177  
photochemical nitrite formation from, 177–181  
photocycloelimination of, 175  
photodissociation into free radicals, 170–172  
photo-induced rearrangement of  $\alpha,\beta$ -unsaturated to  $\alpha$ -oximino-ketones, 177  
preparation of, by alkyl nitrate nitration, 312  
by displacement reactions of alkali metal nitrites, 329–334

- by displacement reactions by nitrite ions, 325-334
- by displacement reactions by silver nitrite, 325-329
- by hydrogenolysis of *gem*-dinitro compounds, 302-304
- from ketoximes, 305
- by nitration of enol esters, with acetyl nitrate, 316-318
- with nitryl chloride, 318-319
- by nitration of olefins, 316-324
- with acetyl nitrate, 316-318
- with dinitrogen tetroxide, 319-320
- with dinitrogen trioxide, 320-323
- with nitric acid, 323-324
- with nitrosyl chloride, 323
- by oxidation of amines, 308-310
- with peracids, 308-310
- by oxidation of *t*-amines with potassium permanganate, 310
- by oxidation of oximes, 306-308
- from oximes, 302-308
- by reaction of active methylene groups with acetone cyanohydrin nitrate, 315-316
- by reaction of active methylene groups with alkyl nitrates, 310-314
- by reaction of active methylene groups with nitrating agents, 310-316
- by reaction of active methylene groups with nitric acid, 314-315
- by reduction of bromonitro compounds, 304-306
- by vapor phase nitration, 302, 340
- primary photochemical processes of, 168-200
- radical anion formation of in photolysis of, 191-192
- Raman spectra of, 80-91
- solvent effects in infrared spectra of, 91
- stereospecificity of the C-N cleavage in hydrogenation of, 303
- aci*-Nitro compounds, see *Nitronic acids*
- 6 $\alpha$ -Nitrocortisone, 324
- 2-(2-Nitro-4-cyanobenzyl)-pyridine, photochromism of, 125
- Nitrocycloalkanes, preparation of from ketoximes, 305
- rate of proton removal from, 370
- $\alpha$ -Nitrocycloalkanones, nmr spectra of, 107
- tautomerism of, 407
- Nitrocyclobutane, preparation of from oxime, 305
- Nitrocyclobutene, 331
- Nitrocyclobutenone, 331
- $\alpha$ -Nitrocyclodecanone, 312
- Nitrocycloheptane, preparation of, by modified Victor Meyer reaction, 332
- by oxidation of oxime, 307
- from oxime, 305
- $\alpha$ -Nitrocycloheptanone, 312
- Nitrocyclohexane, 308, 330
- conformation of nitro group in, 107
- coupling constants of, 108
- $^{14}\text{N}$  chemical shifts in, 110
- nmr spectrum of, 107-108
- preparation of, by oxidation of oxime, 307
- from oxime, 305
- $\alpha$ -proton chemical shift in, 107-108
- 2-Nitro-1,3-cyclohexanediol, nmr spectrum of, 108
- 2-Nitro-1,3-cyclohexanedione, 412
- 2-Nitrocyclohexanol, 317
- trans*-2-Nitrocyclohexanol, 333
- $\alpha$ -Nitrocyclohexanone, 310, 312, 316, 407, 409
- uv spectrum of, 410
- $\alpha$ -Nitrocyclononanone, 312
- $\alpha$ -Nitrocyclooctanone, 311, 312
- 1-Nitro-1,3-cyclopentadiene, 360
- Nitrocyclopentane, 330
- preparation of, by modified Victor Meyer reaction, 332
- by oxidation of oxime, 307
- from oxime, 305
- Nitrocyclopropane, 341
- 2-Nitrocyclopropyl ketone, 341
- trans*-9-Nitrodecalin, 341
- 2 $\alpha$ -Nitrodeoxycorticosterone, 312

- Nitrodesoxyinsitols, 386
- 1-Nitro-3,5-dibenzyl-1,3,5-triazacyclohexane, 651
- Nitrodicyandiamidine, preparation of by nitration of biuret, 624
- 1-Nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, 651
- Nitrodienes, Raman spectra of, 84
- 2-Nitrodimedone, 413
- p*-Nitrodimethylaniline, nitro stretching frequencies of, 85, 87
- 3-Nitro-2,2-dimethylbutane, preparation of from oxime, 305
- 2-Nitro-5,5-dimethylcyclohexane-1,3-dione, 314
- $\beta$ -Nitrodiols, infrared studies of, 112
- p*-Nitrodiphenyl, half-band widths of, 87
- molar extinction coefficients of, 87
- nitro stretching frequencies of, 85, 87
- p*-Nitrodiphenylamine, nitro stretching frequencies of, 85
- 1-Nitro-2,2-diphenylcyclopropane, 341
- 1-Nitro-2,3-epoxybutane, 328, 333
- 3-Nitro-1,2-epoxybutane, 328
- 1-Nitro-2,3-epoxypropane, 328
- $\alpha$ -Nitro esters, from  $\alpha$ -iodoesters with silver nitrite, 328
- preparation of, 315
- by Victor Meyer reaction, 325, 330
- Nitroethane, 325, 365
- esr of, 37-38
- $^{14}\text{N}$  chemical shifts in, 110
- $^{14}\text{N}$  hyperfine coupling constants in radical ions of, 121
- nitro stretching frequencies of, 82
- nmr of, 38
- $n-\pi^*$  transition bands of, 93
- photolysis of, 175
- proton chemical shifts in, 107
- vibrational frequencies of, 82
- 2-Nitroethanol, 333
- Nitroethylene, 341
- bond lengths of, 38-39
- dipole moment of, 38
- electron absorption spectrum of, 39
- microwave spectra of, 38
- nmr spectrum of, 108
- spectroscopic properties of, 38-39
- structure of, 38-39
- 3-Nitroflavanone, 314
- 9-Nitrofluorene, 310
- Nitroformaldehyde phenylhydrazines, electronic absorption spectra of, 102
- 5-Nitro-2-furaldehyde semicarbazone, electronic absorption spectrum of, 103
- 5-Nitrofuran derivatives, Raman spectra of, 88
- Nitrofurans, electronic absorption spectra of, 102-103
- Nitrofurazone, electronic absorption spectrum of, 103
- 5-Nitrofuryl polyenes, electronic absorption spectra of, 102
- Nitrogen dioxide, bond length in, 23
- dipole moment of, 32
- electronic spectrum of, 31, 32
- electronic structure of, 23-32
- electron interactions of, 25-32
- electron spin resonance spectroscopy of, 32
- esr spectrum of, 32
- geometry of, 23-24
- ionization potential of, 25-32
- molecular orbitals of, 25-32
- semiempirical calculations of, 24-25
- Nitro group, activating effect of in nucleophilic displacements, 489-490
- hydrogen bonding with alcohols, 113
- inductive effect in nmr spectroscopy, 106-107
- $n-\pi^*$  transition of, 169-170
- nuclear magnetic spectra of, 106-111
- photochemistry of, 165-202
- spectroscopy of, 167-168
- Nitroguanidine, nitrimino structure of, 674
- x-ray diffraction of, 674
- Nitroguanidines, decomposition of, 626-627
- nitro stretching frequencies of, 88

- o*-Nitrohalobenzenes, relative reaction rates of with various nucleophiles, 495-496
- p*-Nitrohalobenzenes, relative reaction rates of with various nucleophiles, 495-496
- Nitrohalophenols, electronic absorption spectra of, 102
- Nitrohalophenol vinyl ethers, electronic absorption spectra of, 102
- 1-Nitroheptane, preparation of by modified Victor Meyer reaction, 332  
preparation of by oxidation of oxime, 307
- 4-Nitroheptane, preparation of by modified Victor Meyer reaction, 332  
preparation of by Victor Meyer reaction, 327
- 1-Nitrohexane, 308  
<sup>14</sup>N chemical shifts in, 110  
proton chemical shifts in, 107
- 8-Nitrohydindane, 341
- 2-Nitro-1,3-indanedione, 413, 461
- 2-Nitroindane-1,3-dione, preparation of, 314  
transformation with acetic anhydride to acetate of N-hydroxyphthalonimide, 314
- 2-Nitro-1-indanone, 411
- p*-Nitroiodobenzene, nitro stretching frequencies of, 85
- Nitroisoxazoles, electronic absorption spectra of, 102
- 3-Nitro-2-isoxazoline-2-oxide, preparation from 3-bromo-1,1-dinitroalkanes, 431
- Nitroketones, by chromic acid oxidation of nitro alcohols, 314  
tautomeric equilibria composition of, 408
- $\alpha$ -Nitroketones, infrared spectra of, 88
- $\beta$ -Nitroketones, by Victor Meyer reaction, 330
- Nitrolic acid, 394
- Nitrolysis of hexamethylenetetramine, in acetic anhydride and nitrates, 660-670
- in preparation of polynitrimines, 653-670
- Nitromalonaldehyde, 414
- Nitromethane, 307, 325, 334, 424  
C—N stretching frequency of, 89  
dimerization of, 93-94  
dipole moment of, 103  
electron diffraction studies on, 32  
electronic absorption spectrum of, 92  
electronic spectrum of, 34-35  
electronic structure of, 32-34  
emission spectrum of, 125  
hydrogen bonding in, 112  
infrared spectra of, 81  
microwave spectrum of, 106  
molecular orbitals of, 32-34  
nmr of, 38  
*n*- $\pi^*$  transition band of, 92-94, 113  
photolysis of, 170  
proton chemical shifts in, 107  
Raman spectra of, 81  
skeletal and deformation vibrations of, 89  
solvent effect on pmr spectra of, 111  
solvent effects on, 103  
vibrational frequencies of, 82
- Nitromethane-*d*<sub>3</sub> microwave spectrum of, 106  
vibrational frequencies of, 82
- Nitromethanenitronic acid, 358
- 3-Nitro-*p*-menthane, 309
- 2-(Nitromethyl)-alkanenitronic acids, 398
- 2-Nitromethylalkanoic acids, 398
- p*-Nitromethylaniline, nitro stretching frequencies of, 85
- 2-Nitro-3-methylbutane, preparation of by oxidation of oxime, 307
- 3-Nitro-2-methylbutane, preparation of from oxime, 305
- Nitronaphthalenes, nucleophilic displacement reactions of, 579
- Nitronaphthols, electronic absorption spectra of in basic and acidic media, 104
- Nitronate anions, resonance stabilization of, 360

- Nitronate anions (*continued*)  
  stabilization of by hydrogen bonding, 360-361  
  stabilization of by hyperconjugation, 376
- Nitronate salts, C-alkylation of, 417-422  
  O-alkylation of, 417-422  
  factors influencing C-alkylation of, 426-430  
  factors influencing O-alkylation of, 426-430  
  mechanism of in C-alkylation of, 426  
   $\pi$ - $\pi^*$  uv absorption of, 352  
  preparation of from nitroalkanes and metal ethoxides, 460  
  preparation of from nitroalkanes and potassium hydroxide, 460  
  preparation of from nitroalkanes and sodium hydroxide, 460  
  primary, reaction with acylating agents to form trisacylhydroxylamines, 464  
  reaction with diazonium salts, 397-398  
  reaction with epoxides, 451  
  reaction with sulfuric acid, 439
- Nitrones, preparation from nitroso compounds and diazoalkanes, 269-270
- Nitronic acid amides, 469-470
- Nitronic acid anhydrides, 461-468  
  base-catalyzed cleavage of, 467  
  hydrolysis of with sodium hydroxide, 466  
  mechanism of hydroxamic ester formation from, 464  
  mechanism of solvolysis reactions of, 467  
  preparation of from secondary nitronate salts and acid chlorides, 463  
  preparation of from secondary nitronate salts and anhydrides, 463  
  reaction with phenylhydrazine, 466  
  rearrangement of primary to hydroxamic acids, 463  
  solvolysis reactions of, 467
- Nitronic acid esters, physical properties of, 435-437  
  preparation of, 417-435  
  preparation of acyclic, 417-430  
    reactions of, 437-459
- Nitronic acid halides, preparation of, 468-469
- Nitronic acid-nitroalkane mixtures, use of polarography in quantitative analysis of, 472
- Nitronic acids, acidity of, 372  
  addition of dinitrogen tetroxide to, 395-396  
  addition of halogens to, 393  
  addition of hypohalogen acids to, 393  
  addition of iodine monochloride to, 393  
  addition reactions of, 384-398  
  bromine titration of, 471  
  effect of structure on rate of tautomerization of, 355-358  
  electrophilic addition reactions of, 393-398  
  hydrogen halide addition to, 391-392  
  inductive effects on tautomerization rates of, 359-360  
  intramolecular oxidation-reduction in hindered, 401  
  intramolecular proton transfer  
    mechanism of, 355  
  iodine monochloride in quantitative analysis of, 471  
  ionization constants of, 353, 372-376  
  ir spectra of, 383  
  kinetic studies of tautomerism of, 353  
  mechanism for oxidation-reduction of, 400-401  
  mechanism of hydrogen halide addition to, 391-392  
  mechanism of reduction of, 399-400  
  mechanism of tautomerism of, 354  
  nmr spectra of, 383  
  nomenclature of, 350-351  
  nucleophilic addition reactions of, 384-393  
  oxidation of, 398-404  
  oxidation-reduction of, 400-401  
  physical properties of, 382-384  
   $\pi$ - $\pi^*$  uv absorption of, 352  
  p*K<sub>a</sub>* of, 373-376  
  preparation of, 376-382

- preparation of by acidification of a Meisenheimer-type salt, 377
- preparation of by acidification of a nitronate salt, 376-377
- preparation of by addition of anions to olefins, 378
- preparation of by oxidation of oximes, 378-379
- preparation of by photochemical conversion of nitroalkanes, 379
- preparation of from nitronic esters, 379
- products from decomposition of, 387
- properties of, 380-382
- qualitative detection of, 470-473
- quantitative determination of, 470-473
- rates of tautomerization to nitroalkanes, 356-357
- reactions of, 384-417
  - with diazonium salts, 397-395
  - with nitrous acid, 394-395
- reduction of, 398-404
  - to oximes, 398, 399
  - to oximes by hydrogen iodide, 393
- resonance stabilization of, 360
- stereochemistry of *aci*-nitro
  - tautomerism, 363-364
- stereochemistry of hydrogen halide addition to, 392
- tautomerism of, 350, 352-353
- tautomerization to nitroalkanes, 353-364
- uv spectra of, 383
- Nitronic acid salts, preparation of, 459-461
- Nitronic carboxylic acid anhydrides, synthesis of, 462
- Nitronic esters, acid-catalyzed mechanism in isoxazolidine formation, 459
  - acidic and basic hydrolysis of, 438-443
  - catalytic reduction of to amines, 443
  - 1,3-dipolar addition reactions of, 453-459
  - 1,3-dipolar addition to olefins, 453-457
  - hydrolysis of, 437-443
    - to aldehydes and ketones, 438-439
    - to nitroalkanes and alcohols, 438-443
  - hydroxamic acids from, 441
  - ir spectra of, 436
  - mechanism of disproportionation of to carbonyl compounds, 445, 451
  - mechanism of hydrolysis of, 440
  - nmr spectra of, 436
  - oxidation of, 443-453
  - oxidation-reduction reaction of, 444, 446-448
  - $\pi$ - $\pi^*$  uv absorption of, 352
- preparation of, by alkylation of nitronate salts, 417-422
  - by alkylation of silver nitronate salts, 417, 422-423
  - by reaction of iodo or bromotritromethane with olefins, 425
  - by reaction of nitroalkanes with diazomethane, 423-425
  - by reaction of nitronic acids with diazomethane, 423-425
  - by reaction of silver nitronate salts with alkyl halides, 422-423
  - from trialkyl phosphates and ethyl acrylate, 424-425
- preparation of acyclic, 418-421
- preparation of aldehydes and ketones from, 445, 449-450
- preparation of hydroxamic acid chlorides from, 442
- preparation of hydroxamic acid from, 442
- preparation of oximes from, 444, 446-448
- reaction with acid to alcohols, 451
- reaction with sulfuric acid, 439
- reduction of, 443-453
  - with hydrogen iodide to oximes, 443
- synthesis of isoxazolidines from, 454-457
- thermodynamic stability of, 429
- uv spectra of, 435-436
- m*-Nitronitrosobenzene, 279
  - dichroism studies on, 148
  - N=O stretching frequency of, 140
  - $n$ - $\pi^*$  transition of, 148

- o*-Nitronitrosobenzene, 279  
N=O stretching frequency of, 140
- p*-Nitronitrosobenzene, 254  
dipole moment of, 284  
N=O stretching frequency of, 140  
 $n-\pi^*$  absorption data of, 151  
polarographic reduction potentials of, 151
- o*-Nitro-*p'*-nitrosodiphenylamine, 279
- N*-Nitro-*N'*-nitrosopiperazine, electronic absorption spectral data, 154
- 2-Nitro-2-nitrosopropane, N=O stretching frequency of, 140
- 5-Nitronorbornene, 386
- d*-2-Nitrooctane, 354
- t*-Nitrooctane, 308
- 1-Nitrooctane, preparation by modified Victor Meyer reaction, 332  
preparation by oxidation of oxime, 307  
preparation by Victor Meyer reaction, 327
- 2-Nitrooctane, 325, 329  
preparation by modified Victor Meyer reaction, 332  
preparation by Victor Meyer reaction, 327
- Nitro olefins, asymmetric and symmetric stretching frequencies of, 84  
from dehydrohalogenation of  $\beta$ -nitroalkyl iodides, 320  
electronic absorption spectra of, 92-94  
equilibrium composition of, 362  
infrared spectra of, 84  
infrared spectroscopy in polymerization of, 90  
 $\pi-\pi^*$  transition bands of, 94  
Raman spectra of, 84
- Nitroparaffins, C-acylation of primary, 314
- 1-Nitropentane,  $^{14}\text{N}$  chemical shifts in, 110  
preparation of by Victor Meyer reaction, 327  
proton chemical shifts in, 107
- 1-Nitro-3-pentanone, preparation of by modified Victor Meyer reaction, 332
- $\beta$ -Nitroperfluoronitrosoethane, 280  
photolysis of, 286  
pyrolysis of, 286
- Nitrophenanthra-9,10-quinones, benzylic rearrangement of, 597
- 5-Nitro-1,10-phenanthroline, dissociation of in electronic absorption spectroscopy, 105
- p*-Nitrophenetole, electronic absorption spectrum of, 102
- m*-Nitrophenol, far ir spectrum of, 113  
intermolecular hydrogen bonding in, 113  
uv spectrum of, 113
- o*-Nitrophenol, far ir spectrum of, 113  
hydrogen bonding in, 112-116  
infrared spectrum of, 112-113  
intermolecular hydrogen bonding in, 113  
nitro stretching frequencies of, 85  
tautomers of, 415-416  
uv spectrum of, 113
- Nitrophenols, effect of pH on electronic absorption spectra of, 104
- Nitrophenol vinyl ethers, electronic absorption spectra of, 102
- p*-Nitrophenylacetic acid, nitro stretching frequencies of, 85
- 2-Nitrophenylazide derivatives, electronic absorption spectra of, 102
- 2-Nitro-1-phenylcyclohexene, 322
- 3-Nitro-2-phenylcyclohexenone, 322
- 4-Nitro-3-phenylisoxazole, 320
- $\alpha$ -Nitrophenylmethanenitronate, 396
- 3-Nitrophenylmethanenitronic acid, 358, 360  
isomerization of, 351
- p*-Nitrophenylnitromethane, 390
- 4-Nitrophenylnitromethane, 333, 360, 386, 424, 440
- m*-Nitrophenyl phosphate, in nucleophilic photochemical displacement, 582-583

- 1-Nitro-3-phenylpropane, preparation of  
by modified Victor Meyer  
reaction, 332
- 6-Nitropregnenolone acetate, 324
- 2 $\alpha$ -Nitroprogesterone, 312
- 6 $\alpha$ -Nitroprogesterone, 323
- 6 $\beta$ -Nitroprogesterone, 323
- 1-Nitropropane, 314, 325, 390
- <sup>14</sup>N chemical shifts in, 110
- <sup>14</sup>N hyperfine coupling constants in  
radical anions of, 121
- nitro stretching frequencies of, 82
- nmr of, 38
- proton chemical shifts in, 107
- vibrational frequencies of, 82
- 2-Nitropropane, 325
- <sup>14</sup>N chemical shifts in, 110
- <sup>14</sup>N hyperfine coupling constants in  
radical anions of, 121
- nitro stretching frequencies of, 82
- $n-\pi$  transition bands of, 93
- preparation of by Victor Meyer re-  
action, 327
- vibrational frequencies of, 82
- 2-Nitro-1,3-propanediol, 338
- Nitropropene, electron absorption  
spectrum of, 37
- electronic spectrum of, 37
- 1-Nitropropene, nmr spectrum of, 107
- 1-Nitro-1-propene, electron absorption  
spectrum of, 39
- uv absorption spectrum of, 167
- 1-Nitro-2-propene, infrared spectroscopy  
in isomerization of, 90
- 2-Nitro-1-propene, electron absorption  
spectrum of, 39
- 3-Nitropropene, nmr spectrum of, 107
- 3-Nitro-1-propene, electron absorption  
spectrum of, 39
- 3-Nitropropionic acid, natural occur-  
rence of, 333
- $\alpha$ -Nitropropiophenone, 312, 316, 318
- 2-Nitropropiophenone, preparation of  
by modified Victor Meyer  
reaction, 332
- 2-Nitropyridine, electronic absorption  
spectrum of, 102
- 3-Nitropyridine, electronic absorption  
spectrum of, 102
- electronic absorption spectrum of  
anion of, 106
- 4-Nitropyridine, electronic absorption  
spectrum of, 102
- N*-Nitropyrrolidones, electronic absorp-  
tion spectra of, 102
- Nitro salts, bending vibrations of, 90
- infrared spectra of, 88-89
- nitro stretching frequencies of, 88-89
- Nitrosative decarboxylation, kinetics of,  
227-228
- mechanism of, 227-228
- gem*-Nitrosoacetates, 238
- o*-Nitrosoacetophenone, 243
- Nitrosoacetylenes, 274
- 1-Nitrosoacetylenes, preparation of, by  
reaction of nitrosyl chloride with  
an organo mercury compound,  
235
- Nitrosoalkanes, *cis-trans* isomerism in  
dimers of, 149
- dimers of, 14-15
- electronic spectra of, 11-15
- interconversion of isomeric dimers of,  
255
- $n-\pi^*$  transition of, 11-15
- $\pi-\pi^*$  transition of, 11-15
- physical properties of, 10-15
- solvent effects on uv spectra of dimers  
of, 150
- spectral characteristics of, 13
- stability of dimers of, 255
- N*-Nitrosoamides, N=O stretching  
frequency of, 145
- Nitrosoamines, electronic absorption  
spectra of, 152-155
- ir bands of, 145
- N=O stretching frequency of, 144-146
- N*-Nitrosoamines, proton chemical shifts  
in related to carbonium ions, 158
- p*-Nitrosoanisole, 253
- $n-\pi^*$  absorption data of, 151
- polarographic reduction potentials of,  
151
- o*-Nitroso-*o'*-azidobiphenyl, 263



- p*-Nitrosobenzaldehyde,  $n-\pi^*$  absorption data of, 151  
polarographic reduction potentials of, 151
- o*-Nitrosobenzamide, 247
- Nitrosobenzene, 234, 241–242, 244, 252, 262–264, 266–267, 269–270, 275, 278–279, 281, 287  
acid-catalyzed self-condensation of, 272  
from azoxybenzene by pyrolysis, 249–250  
coupling constants of radical anion of, 160–161  
dipole moment of, 53, 284  
electronic absorption spectra of, 148–149  
electronic structure of, 51–54  
enthalpies of dimerization of, 150  
esr spectrum of, 64  
esr spectrum of radical anion of, 160  
irradiation of, 206–207  
microwave spectra of, 161  
 $N=O$  stretching frequency of, 140  
from *N*-phenylbenzalnitrone by photolysis, 249–250  
 $n-\pi^*$  absorption data of, 151  
 $pK_a$  of, 271  
polarographic reduction potentials of, 151  
polarographic reduction to radical anion, 262–263  
radical anion of, 262–263, 282  
Raman study of *cis* dimer, 142  
reaction of, with phosphonium ylides, 278  
with sulfonium ylides, 278  
visible absorption data of, 150
- Nitrosobenzene iron tricarbonyl, 245
- gem*-Nitrosobenzoates, 238
- o*-Nitrosobenzoic acid, 242, 278  
from *o*-nitromandelonitrile, 247  
by photochemical isomerization of *o*-nitrobenzaldehyde, 246
- p*-Nitrosobenzoic acid, 251
- o*-Nitrosobenzophenone, 248
- N*-Nitrosobis-(2,2,2-trifluoroethylamine), electronic absorption spectral data of, 154  
 $N=O$  stretching frequency of, 145
- N*-Nitrosobic (trifluoromethyl)amine, 243
- t*-Nitrosobutane, nmr spectra of dimer of, 159  
nmr spectra of monomer of, 159
- 1-Nitrosobutane, ir absorption of *cis* dimer of, 143  
ir absorption of *trans* dimer of, 143  
solvent effects on uv spectrum of *cis* dimer of, 150  
solvent effects on uv spectrum of *trans* dimer of, 150
- 2-Nitrosobutane, ir absorption of *cis* dimer of, 143  
ir absorption of *trans* dimer of, 143
- N*-Nitrosocarbazole, ir bands of, 145
- Nitrosocarboranes, 234–235
- Nitroso compounds, from  $\alpha$ -branched peroxycarboxylic acids, 228–229  
cleavage of C-nitroso bond of, 284–285  
complexes of with Lewis acids, 274  
complexes of with metal chelates, 274–275  
complexes of with metal salts, 273–274  
conjugate addition reactions of, 286  
Cotton effect of, 155  
deoxygenation of by isonitriles, 263–264  
dimerization of, 252–255  
Ehrlich-Sachs Reaction of, 277–278  
electronic absorption spectra of, 147–155  
enthalpies of dimerization of, 150  
esr spectra of, 160  
fragmentation reactions of, 286–287  
halogen atom expulsion in, 207–208  
 $\alpha$ -halogen displacement in, 260  
hydrogen abstraction in, 206–207  
ir spectra of, 138–147  
isomerization of to oximes, 255–257  
microwave spectra of, 161  
natural occurrence of, 251

- N*-nitroamine formation from, 205–206
- by nitrosation of olefins with nitrites, 229
- by nitrosation of olefins with nitrogen oxides, 230
- by nitrosation of olefins with nitrosamines, 230
- by nitrosation of olefins with nitrosyl chloride, 230–231
- by nitrosation of olefins with nitrosyl sulfuric acid, 232
- by nitrosation of olefins with nitrous acid, 229
- nitroxide formation from, 203–205
- nmr spectra of, 155–160
- oxidation of, 264–265
- photocycloelimination of, 207
- photodissociation of, 203–206
- photolytic disproportionation of, 285–286
- preparation of, by base-catalyzed isomerization of *N*-nitrosohydrazones, 225
- by Baudisch Reaction, 222–223
- by condensation reactions, 250–251
- by dehydrohalogenation of olefin nitrosohalides, 232
- by deoxygenation of nitro compounds, 244–248
- from diazo compounds, 251
- from diazonium compounds, 251
- by electrolysis of oxime salts, 250
- by Fischer-Hepp reaction, 223–225
- from irradiated alkanes and nitrosyl halides, 219–220
- by the Nef reaction, 248–249
- from nitric oxide and radicals, 217–219
- by nitrosation of aromatic ethers, 226–227
- by nitrosation of heterocycles with nitrite esters and alkoxides, 233–234
- by nitrosation of olefins, 229–232
- by nitrosation of phenols, 226
  - by nitrosation of phenols with nitrite esters and alkoxides, 233–234
  - by nitrosation of primary aromatic amines, 225–226
  - by nitrosation of secondary aromatic amines, 223–225
  - by nitrosation of tertiary aromatic amines, 223
  - by nitrosative decarboxylation, 227–229
  - by oxidation of dioximes, 238–240
  - by oxidation of hydroxylamines, 240–241
  - by oxidation of nitrones, 243
  - by oxidation of primary amines, 241–242
  - by oxidation of Schiff bases, 243
  - by oxidation of secondary amines, 242
  - by oxidation of tertiary amines, 243
  - by oxidative nitrosation, 222–223
  - by photolysis of nitrite esters, 220–222
  - by pyrolysis of heterocycles, 249–250
  - by pyrolysis of nitrite esters, 220–222
- from a radical and an olefin, 218–219
- by reaction of organometallics and nitrosyl chloride, 234–235
- by reduction of nitro compounds, 244–248
- pyrolytic disproportionation of, 285–286
- reaction of, with acetylenes, 268
  - with active hydrogen compounds, 271–273
  - with amines, 278–283
  - with arynes, 268
  - with azomethine derivatives, 269
  - with conjugated dienes, 270–271
  - with diazoalkanes, 269–270
  - with free radicals, 265–266
  - with Grignard reagents, 276–277
  - with hydrazines, 278–283
  - with hydroxylamines, 278–283

- Nitroso compounds, reaction of  
 (continued)  
 with methylene groups in carbonyl compounds, 275-276  
 with methylene groups in olefins, 275-276  
 with methylene groups in Schiff bases, 275-276  
 with methynyl groups of carbonyl compounds, 275-276  
 with methynyl groups in olefins, 275-276  
 with methynyl groups in Schiff bases, 275-276  
 with monoolefins, 266-268  
 with phenols, 272  
 with phosphorous ylids, 268  
 with thioketones, 268  
 reduction of, 260-263  
 reduction paths of, 261  
 reductive alkylation of, 262  
 solvent effects of in addition of nitrosyl chloride to olefins, 231-232  
 steric inhibition of resonance by ortho effects in monomers, 254  
 ultraviolet spectroscopy of, 202  
 visible absorption data of, 150
- C-Nitroso compounds, diamagnetism of, 252  
 nmr spectra of dimers of, 159  
 N=O stretching frequency of, 140  
 N=O stretching vibration frequency of, 139-144  
 paramagnetic resonance absorption of, 252
- gem*-Nitrosocyanides, pyrolysis of, 285
- 4-Nitrosocycloheptanol, 222
- Nitrosocyclohexane, 241  
 enthalpies of dimerization of, 150  
 N=O stretching vibrations of, 139, 140  
 Raman study of *trans* dimer, 142  
 visible absorption data of, 150
- 4-Nitrosocyclooctanol, 222
- o*-Nitroso-*N,N*-dimethylaniline, 277
- p*-Nitrosodimethylaniline, 258, 272, 278, 283  
 dipole moment of, 284  
 $pK_a$  of, 284
- p*-Nitroso-*N,N*-dimethylaniline, 223, 274, 280
- p*-Nitroso-*N,N*-dimethylaniline ferro-cyanide, 273
- 3-Nitroso-2,5-dimethylpyrrole, 233
- 1-Nitroso-3,5-dinitro-1,3,5-triazacyclohexane, 669
- N*-Nitrosodiphenylamine, ir bands of, 145
- p*-Nitrosodiphenylamine, 244, 279
- gem*-Nitrosoesters, preparation of from oximes, 238
- Nitrosoethane, ir absorption of *cis* dimer of, 143  
 solvent effects on uv spectrum of *cis* dimer of, 150  
 solvent effects on uv spectrum of *trans* dimer of, 150
- 1-Nitroso-2-*N*-ethylaminonaphthalene, 279
- N*-Nitrosoethylaniline, ir bands of, 145
- p*-Nitroso-*N*-ethylanthranilic acid, from *N*-ethylanthranilic acid, 225
- Nitroso group, activation of  $\alpha$ -substituents by, 259-260  
 as activator in nucleophilic displacement reactions, 283-284  
 base-catalyzed condensations of, 277-278  
 1,5-migration of (Barton reaction), 221-222  
 photochemistry of, 202-208  
 primary photochemical processes of, 203-208  
 spectroscopy of, 137-161
- Nitrosoguanidines, N=O stretching frequency of, 145
- gem*-Nitrosohalides, preparation of from oximes, 235-238
- 7-Nitrosoheptanal, 222
- 1-Nitrosohexyne-1, 266
- Nitrosohydroxylamine, ir spectra of, 146  
 N-N stretching frequency of, 146  
 N=O stretching frequency of, 146
- 3-Nitrosoindole, 233

- Nitrosoisopropylacetone, photocyclo-  
elimination of, 207
- Nitrosomesitylene, 269  
N=O stretching frequency of, 140
- Nitrosomethane, 256, 266  
from *t*-butyl nitrite, 220  
dimer of, 252  
geometry of, 10–11  
ir absorption of *cis* dimer of, 143  
ir absorption of *trans* dimer of, 143  
nmr spectra of *cis* dimer of, 159  
nmr spectra of *trans* dimer of, 159  
N=O stretching vibrations of, 139,  
140  
solvent effects on uv spectrum of *cis*  
dimer of, 150  
solvent effects on uv spectrum of  
*trans* dimer of, 150
- N*-Nitrosomethylaniline, ir bands of,  
145
- 2-Nitroso-2-methylpropane, 243
- 1-Nitroso-2-naphthol, 279  
cobalt chelate of, 274
- m*-Nitrososobenzene, N=O stretch-  
ing frequency of, 140
- 2-Nitroso-3-nitro-*p*-xylene, 249
- Nitrosonium ion, stretching frequency  
of, 138
- 1-Nitrosopentane, solvent effects on uv  
spectrum of *cis* dimer of, 150  
solvent effects on uv spectrum of  
*trans* dimer of, 150
- o*-Nitrosophenol, 257  
solvent effects on the electronic ab-  
sorption spectrum of, 152
- p*-Nitrosophenol, 257, 273, 284  
*n*- $\pi^*$  absorption data of, 151  
polarographic reduction potentials of,  
151
- Nitrosophenols, chelates of, 274  
ir studies on, 143
- p*-Nitroso-*N*-phenyl-*N*-methylaniline,  
223
- Nitrosopiperazines, ir data of, 146
- N*-Nitrosopiperidine, electronic absorp-  
tion spectral data of, 154  
ir bands of, 145
- 1-Nitrosopropane, solvent effects on uv  
spectrum of *cis* dimer of, 150  
solvent effects on uv spectrum of *trans*  
dimer of, 150
- 2-Nitrosopropane, solvent effects on uv  
spectrum of *cis* dimer of, 150  
solvent effects on uv spectrum of *trans*  
dimer of, 150
- $\beta$ -Nitrosopyrroles, 257
- $\beta$ -Nitrosostyrene, 232
- $\alpha$ -Nitrosotoluene, 256  
dimer of, 253  
nmr spectra of dimer of, 159
- p*-Nitrosotoluene, 252, 272, 278  
*n*- $\pi^*$  absorption data of, 151  
polarographic reduction potentials of,  
151
- Nitrosotrifluoromethane, 249
- N*-Nitrosourethanes, nmr spectra of, 158
- o*-Nitrostilbene, nitro group participa-  
tion in photocycloaddition of,  
195–197
- $\alpha$ -Nitrostyrene, preparation of by Victor  
Meyer reaction, 327
- $\beta$ -Nitrostyrene, 199  
cycloaddition of with olefins, 176–177  
photodimerization of *trans* isomer of,  
176  
photolysis of *trans* isomer of, 175
- Nitrosyl chloride, *n*- $\pi^*$  transition of, 148  
 $\pi$ - $\pi^*$  transition of, 148  
use of as nitrating agent, 323
- Nitrosyl halides, N=O stretching fre-  
quency of, 138
- 6 $\alpha$ -Nitrotestosterone, 323, 324
- 6 $\beta$ -Nitrotestosterone, 323
- 2-Nitro- $\alpha$ -tetralone, 312, 410
- 2-Nitro-1-tetralone oxime, 322
- Nitrothiophene derivatives, electronic  
absorption spectra of, 102
- o*-Nitrotolan, nitro group participation  
in photocycloaddition of, 197–198
- m*-Nitrotoluene, nitro stretching fre-  
quencies of, 85
- o*-Nitrotoluene, 355  
mechanism of photolysis of in hydro-  
gen abstraction, 182  
nitro stretching frequencies of, 85

- p*-Nitrotoluene, 355  
 coupling constants of, 109  
 esr spectra of radical anions of, 122–123  
 nitro stretching frequencies of, 85  
 pmr spectra of, 109  
 proton chemical shifts of, 109
- Nitrotoluidines, nmr spectra of, 109
- Nitrotribromomethane, electron diffraction studies on, 32
- Nitrotrichloromethane, nitro stretching frequencies of, 82  
 $n-\pi^*$  transition bands of, 93
- Nitrotrifluoromethane, electron diffraction studies on, 32  
 nitro stretching frequencies of, 82  
 $n-\pi^*$  transition bands of, 93
- Nitrourea, decomposition of, 625
- Nitroureas, nitro stretching frequencies of, 88  
 preparation of from aliphatic primary nitramines and isocyanates, 623
- Nitrourethane, nmr spectrum of, 674
- $\gamma$ -Nitrovaleric acid, 333
- Nitrovinilation reaction, preparation of 4-keto-1-nitroolefins by, 414–415
- bis*-Nitroxyethylnitramine, x-ray diffraction of, 674
- bis*-Nitroxyethylnitrooxamide, preparation of, 639–640
- Nitro-*p*-xylene, pmr spectra of, 109
- Nitroxyl radical, 251, 256
- bis*-Nitroxymethylnitramine, 656
- Nitryl chloride, use of as nitrating agent, 318–319
- Nuclear magnetic resonance spectra, of  
 nitro group, 106–111  
 of nitroso compounds, 155–160
- Nuclear magnetic resonance spectroscopy, of aromatic nitro compounds, 54–58  
 of aromatic nitroso compounds, 54–58  
 of dinitromethane, 38  
 of nitroalkanes, 38  
 of 1-nitrobutane, 38  
 of nitroethane, 38  
 of nitromethane, 38  
 of 1-nitropropane, 38  
 of trinitromethane, 38
- Nuclear magnetic resonance spectrum, of nitramine, 674  
 of nitrourethane, 674
- Nucleophilic addition reactions, of  
 nitronic acids, 384–393
- Nucleophilic aromatic substitution, addition–elimination mechanism in, 490  
 elimination–addition mechanism in, 490  
 $S_N1$ -mechanism in, 491
- Nucleophilic displacements, activating effect of nitro group in, 489–490  
 of alkoxy groups, by amines in  
 nitroaromatics, 569–572  
 in *trans*-etherification in nitroaromatics, 565–568  
 in hydrolysis in nitroaromatics, 565–568  
 by mercaptides in nitroaromatics, 571  
 of amino groups from nitroaromatics, 574–575  
 of ammonium groups from nitroaromatics, 574–575  
 of aryloxy groups, by amines in nitroaromatics, 569–572  
 in *trans*-etherification of nitroaromatics, 565–568  
 in hydrolysis of nitroaromatics, 565–568  
 by mercaptides in nitroaromatics, 571
- deactivation factors of halogens in halonitrobenzenes, 538–539  
 effect of substituents in the substrate on, 536–540  
 of ester group from aromatic nitrocarboxylates, 572–573  
 of halogens from nitrohalobenzenes by halogens, 512–514  
 from halonitrobenzenes by mercaptide and thiophenolate anions, 515  
 from *o*-halonitrobenzenes by methoxide ions, 536

- in heterocyclic nitrocompounds, 581–582
  - of hydrogen in nitroaromatics, 554–561
  - influence of carbonyl group on in halonitrobenzenes, 537
  - influence of polarizability on halonitrobenzenes in, 549
  - intramolecular hydrogen bonding in fluoronitrobenzenes, 529–530
  - isotope effects in nitroaromatics, 530–531
  - kinetics of two-step mechanism of, 520–530
  - nature of intermediate complexes in, 531–536
  - nature of transition states in, 531–536
  - of nitro groups in nitroaromatics, 561–565
  - from nitrohalobenzenes, by alkoxy- and phenoxyanions, 512
  - by amines, 499–506
  - by azide and thiocyanate anions, 515
  - by carbanions, 515–516
  - by hydroxide or water, 507–512
  - by sulfides, 514
  - by sulfite, carboxylate, and thio-sulfone, 516–517
  - of phosphate group from aromatic nitrophosphates, 572–573
  - in polycyclic nitrocompounds, 578–581
  - rate of halogen displacement, from halodinitrobenzenes, 578
  - from halodinitronaphthalenes, 578
  - rates in base catalysis on the reactions of substituted nitrobenzenes with amines, 522–527
  - reactions of, nitroanthracenes, 579
  - nitronaphthalenes, 579
  - reactivity of, leaving group in, 542–548
  - nucleophiles in, 549–552
  - relative leaving abilities for various substituents in nitroaromatics, 543
  - relative rates of displacement of halogen from halonitrobenzenes in, 544–545
  - relative reactivities of nucleophiles with fluoro- and iodonitrobenzenes, 550
  - relative reactivities for various nucleophiles with halonitrobenzenes, 547, 548
  - solvent effects on the rate of reaction in, 552–554
  - steric effects in, 540–542
  - substituent effects in nucleophilic reagents correlated by the Hammett equation in halonitrobenzenes in, 551
  - of substituted nitroaromatics, 575–577
  - of sulfonate groups from aromatic nitrosulfonates, 572–573
  - transition state of one stage mechanism, 519
  - transition states of two stage mechanism, 519
- Nucleophilic photochemical displacement, of alkoxy groups in nitroaromatics, 582–585
- of halogen from halonitroaromatics, 585–586
  - of nitro groups from nitroaromatics, 586–587
- Nucleophilic photosubstitutions, via  $\pi-\pi^*$  excited singlet state, 584–585
- of *m*-nitrophenyl esters, 584
  - of *m*-nitrophenyl ethers, 584
- Nucleophilic substitution, in aromatic systems, 489
- displacement reactions of halonitrobenzenes, 492–518
  - energy diagram of aromatic, 520
  - kinetics of, 518–554
  - mechanism of, 518–554
  - one stage mechanism of, 518–520
  - two stage mechanism of, 518–520
- O**
- Octane-2-nitronic acid, 362
  - Organic nitrites, N=O stretching vibration frequency of, 139
  - Orton rearrangement, 616

- Oxidation, of nitronic acids, 398–404
  - of nitronic esters, 443–453
  - of nitroso compounds, 264–265
  - of oximes to nitro compounds, 306–308

Oxidative nitration, see *Kaplan-Shechter reaction*

Oximes, conversion to nitro compounds, 302–308

from nitroso compounds by isomerization, 255

oxidation of to nitro compounds, 306–308

$\alpha$ -Oximinoketones, formation of by photo-induced rearrangement of  $\alpha,\beta$ -unsaturated nitro compounds, 177

Oxindigos, 410–411

## P

Pentafluoronitrosoethane, pyrolysis of, 285

Pentamethylnitrosobenzene, 234

Peracetic acid, use in oxidation of amines, 308–309

Peracids, use in oxidation of amines, 308–310

Perbenzoic acid, use in oxidation of amines, 308

Perfluoronitrosoalkanes, reversible photochemical dimerization of, 285

Perfluoronitrosomethane, irradiation of, 205–206

Perfluoro 2-nitroso-2-methylpropane, 285

Peroxytrifluoroacetic acid, preparation of, 308

use in oxidation of oximes, 306–308

Phenylazonitronic acid, 398

Phenylchloronitrosomethane, 392

Phenyl-1,2-diaminoethane, 443

Phenyldinitromethane, 338

Phenylmethanenitronic acid, 360, 362, 392, 424

ionization constant of, 353–354

mechanism of reaction of with acyl chlorides to hydroxamic acid chloride, 465

reaction of, with acetyl chloride to hydroxamic acid chloride, 465

with benzoyl chloride to hydroxamic acid chloride, 465

Phenylnitramine, reaction of with nitrous acid, 621

Phenyl nitrene, 263

$\alpha$ -Phenylnitroethane, preparation of by oxidation of oxime, 307

1-Phenyl-2-nitroethanol, 307

Phenylnitromethane, 310, 314, 334, 338, 379

nitro stretching frequencies of, 82

preparation of by modified Victor

Meyer reaction, 332

3-Phenyl-1-nitropropane, 424

1-Phenyl-2-nitropropene, photolytic isomerization of, 221

Phenylnitrosomethane, enthalpies of dimerization of, 150

visible absorption data of, 150

1-Phenyl-1-nitroso-2-nitropropane, 229

Phenylpseudonitrole, 395, 396

Photochemical displacement, of alkoxy groups in nitroaromatics, 582–585  
of halogen from halonitroaromatics, 585–586

of nitro groups from nitroaromatics, 586–587

Photochemistry, of nitro group, 165–202  
of nitroso group, 202–208

Photolysis, of methyl *o*-nitrosobenzoate, 286

of nitrite esters, 220–222

of  $\beta$ -nitroperfluoronitrosoethane, 286

of *N*-phenylbenzalnitro to nitroso-benzene, 249–250

Photolytic disproportionation, of nitroso compounds, 285–286

Physical properties, of nitramines, 670–680

Picric acid, electronic absorption spectrum of, 106

Polarography, of nitroalkanes, 372

of nitronic acids, 372

use of in quantitative analysis of nitronic acid–nitroalkane mixtures, 472

Polycyclic nitrocompounds, nucleophilic displacements in, 578–581

- Polynitrimines, 649-670  
  from acetic anhydride, nitrates, and  
    hexamethylenetetramine, 660-670  
  electrical polarization of, 675-680  
  preparation of from nitric acid and  
    hexamethylenetetramine, 651-660  
  X-ray diffraction of, 674
- Polynitroamines, nitro stretching  
  frequencies of, 88
- Polynitroaromatics, Meisenheimer com-  
  plexes from the reaction of with  
    diazomethane, 595  
  reaction of with diazomethane, 595  
  ring enlargement of, 595-597
- Polynitrobenzenes, rates of reaction of  
  with aniline, 562
- Polynitro compounds, by oxidative  
  nitration, 336-339  
  preparation of, 334-340  
    by alkyl nitrate nitration, 335  
    by conversion of olefins, 335  
    by internal displacement reactions,  
      339-340  
    by Kaplan-Shechter reaction, 336-  
      339  
    by oxidation of diamines, 335  
    by oxidation of pseudonitroles, 339  
    by ter Meer reaction, 335-336  
    by Victor Meyer reaction, 335
- Potassium fluorene-9-nitronate, 379, 452
- Potassium indene-1-nitronate, 415
- Potassium 1-nitroethanenitronate, 396,  
  467
- Potassium 1-nitromethanenitronate, 467
- Potassium trinitromethane, 425
- Potentiometric titrations, of nitro-  
  alkanes, 372  
  of nitronic acids, 372
- Primary isonitramines, 619-623  
  tautomerism in, 619-620
- Primary nitramides, 624-627  
  from nitrimides by isomerization in  
    alkali, 641-643  
  preparation of, 624  
    by nitration of urea, 624
- Primary nitramines, 614-619  
  acidity of, 618  
  aliphatic reaction with isocyanates  
    to nitroureas, 623  
  hydrogenolysis of, 623  
  physical properties of, 617-618  
  preparation of, by alkaline hydrolysis  
    of nitramides, 615-616  
    from dichloroamines, 617  
    by oxidation of salts of diazotates,  
      616  
    by reaction of ethyl nitrate with  
      amines in base, 616-617  
  reaction with diazomethane, 620  
  reaction with nitrous acid, 620-621  
  reduction of aromatic, 622-623  
  tautomerism in, 618
- Primary photochemical processes, of  
  nitro compounds, 168-200
- 1,3-Propanebisnitronic acid, intra-  
  molecular hydrogen bonding in,  
  372
- Propane-2-nitronic acetic anhydride,  
  hydrolysis of, 466
- Propane-1-nitronic acid, 362
- 1-Propionyl-3,5,7-trinitro-1,3,5,7-tetraza-  
  cyclooctane, 668
- o*-i-Propylnitrobenzene, electronic ab-  
  sorption spectrum of, 99
- p*-i-Propylnitrobenzene, electronic ab-  
  sorption spectrum of, 97
- p*-*n*-Propylnitrobenzene, electronic ab-  
  sorption spectrum of, 101
- N*-i-Propyl-*N*-phenylnitrosamine, chemi-  
  cal shifts of, 157
- Pseudonitrole, mechanism for formation  
  of, 394  
  stereochemistry for formation of, 394-  
  395
- Pyridine N-oxide, dipole moment of,  
  64-65  
  electron absorption spectrum of, 65-66  
  electronic structure of, 64-68  
  *n*- $\pi^*$  transitions of, 66
- Pyridyl nitrophenylmethanes, 379
- Pyrolysis, of azoxybenzene to nitroso-  
  benzene, 249-250  
  of heterocycles to nitroso compounds,  
    249-250  
  of nitrite esters, 220-222



Pyrolysis (*continued*)

- of  $\beta$ -nitroperfluoronitrosoethane, 286
- of *gem*-nitrosocyanides, 285
- of pentafluoronitrosoethane, 285
- of trifluoronitrosomethane, 285

## Pyrolytic disproportionation, of nitroso compounds, 285–286

**R**

## Radical anions, in C-alkylation of nitronate salts, 426

- esr spectroscopy of, 121–125
- as intermediates in reduction of nitronic acids, 399–400
- of nitroalkanes, 37–38
- of nitroaromatic compounds, 58–64

## Radical substitution, in aromatic systems, 489

## Raman spectra, of aromatic nitro compounds, 85–88

- of heterocyclic nitro compounds, 85–88
- of *N*-methylphenylnitramine, 670
- of nitramines, 670–673
- of nitrobenzene, 70
- of nitro compounds, 80–91
- of nitrodienes, 84
- of nitro-olefins, 84

## Rates of reaction, of halogen displacement from halodinitrobenzenes, 578

- of halogen displacement from halodinitronaphthalenes, 578
- of polynitrobenzenes with aniline, 562

## RDX, 657

## Reaction rates, relative, of 2,4-dinitro- and 4-nitrohalobenzenes with etoxide and piperidine, 494

- of *o*- and *p*-nitrohalobenzenes with various nucleophiles, 495–496

## Rearrangement reactions, of nitroaromatics, 587–598

- of polynitroaromatics, 595–597
- von Richter reaction, 591–595

## Reduction, of nitro compounds, 244–248

- of nitronic acids, 398–404

## of nitronic esters, 443–453

## of nitroso compounds, 260–263

sodium borohydride of *gem*-halonitro compounds, 304

## Ross-Schiessler process, 661

**S**

## Salt of nitromethane, infrared spectra of, 89

## Salts of 1,1-dinitroalkanes, infrared spectra of, 89

Salts of  $\alpha$ -nitroketones, infrared spectra of, 89Salts of  $\alpha$ -nitronitriles, infrared spectra of, 89

## Sanger reagent, 499

## Saturated nitro compounds, asymmetric stretching frequencies of, 81–84

## Secondary isonitramines, 637–639

- preparation of by alkylation of primary nitramines, 637–638

## reaction of with sulfuric acid, 638–639

## Secondary nitramides, 639–645

- preparation of by reaction of amides with nitric acid, 639–641

## Secondary nitramines, 628–637

- chain reaction mechanism in nitration of amines, 635

## effect of chloride ion in preparation of, 634–637

## influence of basicities of amines in preparation of, 630

## mechanism of preparation of by acidic nitration of amines, 631

## preparation of, 628

## preparation of by acidic nitration of amines, 631

## preparation of by nitration of chloramines, 636

## preparation of by nitration–oxidation of aromatic amines, 628–637

## preparation of from amines, 633

## preparation of from nitrosoamines, 633

## from primary nitramines by Michael reaction, 633

- Semicarbazones, nmr spectra of, 108-  
Semiempirical calculations, of nitrogen dioxide, 24  
Silver dinitromethanenitronate, C-alkylation of, 428  
Silver nitrocyanomethanenitronate, O-alkylation of, 428  
Silver 1-nitroethanenitronate, 445  
Silver nitronate salts, use of in preparation of nitronic esters, 460  
Silver phenylmethanenitronate, C-alkylation of, 429  
Silver picrate, 423  
Smiles rearrangement, mechanism of, 587-588  
    of nitroaromatics, 587-591  
 $S_N1$ -mechanism, in nucleophilic aromatic substitution, 491  
Sodium bicyclo(2.2.1)-heptane-2-nitronate, 395  
Sodium borohydride, 311  
    reduction of *gem*-halonitro compounds with, 304  
Sodium butane-2-nitronate, 438  
Sodium cyclohexanenitronate, 422  
Sodium cyclopentanenitronate, 422  
Sodium ethanenitronate, 464  
Sodium methanenitronate, deformation vibrations of, 90  
Sodium *p*-nitrophenoxide, nitro stretching frequencies of, 85  
Sodium 3-nitropropionate, 333  
Sodium phenylmethanenitronate, 379, 464  
Sodium propane-2-nitronate, 339, 422  
    C-alkylation of, 427  
    O-alkylation of, 427  
Solvation, effect on rate of chlorine displacement from nitroaromatics, 498  
Solvent effects, on the rate of reaction in nucleophilic displacements, 552-554  
Spectroscopy, of hydrogen bonding, 112-116  
    of keto-enol equilibria, 112-116  
    of nitro group, 167-168  
    of nitroso group, 137-161  
    of proton removal from nitrocyclohexanes, 370  
Steric effects, effect of on rate of proton removal of nitroalkanes, 367-370  
Steric interactions, in electronic absorption spectra, 96, 100  
Substituted nitrobenzenes, electronic properties of, 48-51  
    solvent effects on electronic absorption spectra, 103  
Substitution reactions, of aromatic nitroso compounds, 283-284  
Sydnones, N=O stretching frequency of, 145
- T**
- ter Meer reaction, 404  
    mechanism of, 335-336  
    preparation of polynitro compounds by, 335-336  
1,1,4,4-Tetrabromo-1,4-dinitrobutane, 311  
3,6-Tetrahydrooxazines, 249  
2,3,5,6-Tetra-*iso*-propyl-1-nitrobenzene, infrared spectrum of, 87  
2,3,5,6-Tetramethylnitrobenzene, esr spectrum of, 63  
 $\alpha, \alpha, \omega, \omega$ -Tetranitroalkanes, preparation of by ter Meer reaction, 335  
1,1,4,4-Tetranitrobutane, 335, 338, 404  
1,1,7,7-Tetranitroheptane, 338  
1,1,6,6-Tetranitrohexane, 338  
Tetranitromethane, charge-transfer complexes with aromatic hydrocarbons, 119  
     $^{14}\text{N}$  chemical shifts in, 110  
1,4,5,8-Tetranitronaphthalene, esr spectrum of, 63  
1,1,1,3-Tetranitropropane, 340  
1,1,3,3-Tetranitropropane, 340  
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane, 657  
TETRYL, 640  
Transition states, nature of in nucleophilic displacements, 531-536  
Trialkyl phosphites, use of in preparation of nitronic esters, 424-425

- 2-*H*-1,2,3-Triazole-1,3-dioxide, 470
- 2,4,6-Tribromonitrosobenzene, enthalpies of dimerization of, 150
- N=O stretching frequency of, 140
- visible absorption data of, 150
- Trichloronitrosomethane, 222
- N=O stretching frequency of, 140
- Trifluoroethyl nitrite, N=O stretching vibration frequency of, 139
- o*-Trifluoromethylnitrobenzene, nitro stretching frequencies of, 85
- m*-Trifluoromethylnitrosobenzene, 244, 265
- Trifluoronitrosomethane, 222, 263, 265, 267, 269, 271
- ir spectrum of, 145
- N=O stretching frequency of, 140
- n*- $\pi^*$  transitions of, 69
- pyrolysis of, 285
- Trihydroxymethylnitrosomethane, dissociation of, 286-287
- 2,4,5-Trimethoxynitrosobenzene, 259
- 2,2,4-Trimethyl-5-nitrocyclopentanone, 312
- Trimethylamine N-oxide, dative bond in, 22-23
- dipole moment of, 22, 64-65
- N-O bond length of, 22-23
- uv spectrum of, 23
- 2,4,6-Trimethylnitrosobenzene, enthalpies of dimerization of, 150
- visible absorption data of, 150
- sym*-Trinitrobenzene, 201
- charge-transfer interaction with aromatic hydrocarbons, 117-118
- charge-transfer spectrum of with naphthalene, 117
- electronic absorption spectrum of, 96
- 1,3,5-Trinitrobenzene, 414
- coupling constants of, 109
- visible spectra of with sodium methoxide, 106
- Trinitrobenzene derivatives, electronic absorption spectra of in alkaline solutions, 106
- 1,3,5-Trinitrobenzene derivatives, infrared data of, 90
- Trinitrobenzenes, solvent effects on electronic absorption spectra, 103
- Trinitromethane, electronic absorption spectrum of, 94
- $^{14}\text{N}$  chemical shifts in, 110
- nmr of, 38
- proton chemical shift in, 107
- Trinitromethyl carbinols, determination of dissociation of in electronic absorption spectroscopy, 104
- 2,4,6-Trinitrophenol, coupling constants of, 109
- N*-1,3,5-Trinitrosophenyl-*N'*-phenylhydrazine, 245
- Trinitrosophloroglucinol, 226
- 1,3,5-Trinitroso-1,3,5-triazacyclohexane, electronic absorption spectral data of, 154
- from hexamethylenetetramine and nitrous acid, 668-669
- Trinitrotoluene, 377
- 3,4,5-Triphenyl-2-isoxazoline-2-oxide, 431
- Triphenyl phosphine, see *Deoxygenation*
- Triphenylphosphonium methylide, as alkylating agent in nucleophilic displacement of nitroaromatics, 556
- Tripotassium 1,3,5-triazacyclohexane-1,3,5-trisulfonate, 670
- Trisacylhydroxylamines, 464

## U

- Ultraviolet spectra, see also *Electron absorption spectra*
- of nitramines, 673
- Ultraviolet spectroscopy, of nitroso compounds, 202

## V

- Valence bond calculations, 533
- Valence electrons, discussion of, 3-4
- Vibrational spectra, of nitramines, 670-673

Victor Meyer reaction, 310, 325-329, 390  
  experimental conditions for, 328-329  
  experimental conditions for modification of, 334  
  mechanism of, 325-326  
  stereochemistry of, 325-326  
von Richter reaction, 247, 563  
  mechanism of, 592-595  
  of nitroaromatics, 591-595

### X

X-ray diffraction, of 1-acetyl-3,5,7-tri-  
  nitro-1,3,5,7-tetrazacyclooctane,  
  674  
  of cyclonite, 674  
  of ethane-1,2-dinitramine, 674

  of nitramines, 674  
  of nitroguanidine, 674  
  of *bis*-nitroxyethylnitramine, 674  
  of polynitrimines, 674

### Y

Yanowski reaction, nucleophilic displacement of hydrogen in nitroaromatics, 559-561

### Z

Zimmermann reaction, nucleophilic displacement of hydrogen in nitroaromatics, 559-561